

SAN JOSE/SANTA CLARA WATER POLLUTION CONTROL PLANT MERCURY FATE AND TRANSPORT STUDY



Submitted to:

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Table of Contents

Executive Summary	ES-1
1.0 Introduction.....	1-1
1.1 Mercury in Wastewater Treatment Plants	1-2
1.2 Overview of Plant Operation	1-5
1.3 Report Organization.....	1-9
1.4 References	1-9
2.0 Sampling Objectives	2-1
2.1 Understand the Mechanisms of Mercury Removal in Different Process Operations	2-1
2.2 Characterize the Concentration and Form of Mercury at Various Locations Under a Range of Representative Operating Conditions	2-2
2.3 Develop a Mass-Balance for Mercury	2-2
2.4 Two-Phased Approach for Data Collection	2-2
3.0 Sampling Locations and Analysis Methods.....	3-1
3.1 Sampling Locations and Frequency.....	3-1
3.2 Parameters and Analytical Methods for Wastewater, Sludge, and Air Samples	3-4
3.3 Water Sampling Procedures	3-6
3.3.1 Mercury Water Sampling.....	3-6
3.3.2 Water Sampling for Ancillary Water Quality Parameters	3-6
3.3.3 Measurement of Field Parameters.....	3-8
3.4 Sludge Sampling Procedures	3-8
3.5 Quality Assurance/Quality Control (QA/QC) Procedures	3-8
4.0 Results	4-1
4.1 Mercury Species in Aqueous Phases	4-1
4.2 Mercury Species in Sludge	4-6
4.3 Ancillary Parameters.....	4-11
4.4 24-Hour Sampling Results	4-13
4.5 Comparison of Composite and Grab Samples.....	4-15
4.6 Mass Balance Calculations.....	4-16
4.7 Mercury Load Variation and Estimation of Unaccounted Mass.....	4-18
4.8 Correlations of Mercury with Other Parameters	4-24

4.9	Trend Analysis of Mercury Concentration	4-28
4.10	Findings Related to the Key Study Questions.....	4-30
4.11	Summary	4-32
5.0	Conclusions and Lessons Learned	5-1
5.1	Understand mercury removal mechanisms in different Plant process operations	5-1
5.2	Characterize mercury concentration and form of at various Plant locations under a range of representative operating conditions	5-1
5.3	Develop a Plant mass-balance to identify critical stages in the process and sinks for mercury	5-2
5.4	Develop a two-phased approach to data collection, with a screening phase, and a second phase for more detailed analysis of specific components	5-2
5.5	Final Conclusions.....	5-2
5.6	Lessons Learned	5-3
5.6.1	Wastewater Treatment:	5-3
5.6.2	Analytical Measurement:	5-4
Appendix A	Uncertainty Analysis of Summing and Multiplying Measurement Variables.....	A-1
Appendix B	Confidence Interval for the Mean	B-1
Appendix C	Mann-Kendall Test of Slope for Trend Significance and the Seasonal Kendall Test.....	C-1

List of Figures

Figure 1-1	Location of San Jose/Santa Clara Water Pollution Control Plant and other major treatment plants in South San Francisco Bay.	1-2
Figure 1-2	Range of total mercury concentrations in natural waters and untreated and treated wastewater	1-3
Figure 1-3	Range of methylmercury concentrations in surface waters and untreated and treated wastewater	1-4
Figure 1-4	Mercury reactions in aquatic systems with emphasis on reactions that may effect wastewater treatment	1-5
Figure 1-5	Simplified process diagram of San Jose/Santa Clara Water Pollution Control Plant.....	1-7
Figure 1-6	Schematic of single stage activated sludge processing basin.....	1-7
Figure 1-7	Daily average influent flow to Primary and volumes treated in the “Nitrification” and “Secondary” process paths.	1-8
Figure 1-8	Daily average effluent flow	1-8
Figure 3-1	Process flow diagram for San Jose/Santa Clara Water Pollution Control Plant with sampling locations identified	3-3
Figure 4-1	Total mercury in the San Jose/Santa Clara Water Pollution Control Plant.....	4-4
Figure 4-2	Dissolved mercury in different Plant process steps.....	4-5
Figure 4-3	Total unfiltered methylmercury in different Plant process steps.	4-5
Figure 4-4	Mercury concentrations in sludge at different Plant locations.	4-7
Figure 4-5	Methylmercury concentrations in sludge at different Plant locations	4-8
Figure 4-6	Total mercury concentrations in different quads of the activated sludge process.....	4-9
Figure 4-7	Methylmercury concentrations in different quads of the activated sludge process.....	4-10
Figure 4-8	Dissolved oxygen concentrations at different Plant locations.....	4-11
Figure 4-9	pH levels at different Plant locations	4-12
Figure 4-10	Total suspended solids (TSS) at different Plant locations	4-12
Figure 4-11	Chloride at different Plant locations.....	4-13
Figure 4-12	Sulfate at different Plant locations.....	4-13
Figure 4-13	Mercury species and TSS concentrations at different sampling times during the day.....	4-14
Figure 4-14	Total and methylmercury concentrations in the final effluent at different sampling times.	4-15

Figure 4-15	Comparison of total mercury concentrations from grab samples and from 24-hour composite samplers.	4-16
Figure 4-16	Mass balance for total mercury in the Plant	4-17
Figure 4-17	Mass balance for methylmercury in the Plant.....	4-18
Figure 4-18	Schematic of daily average loads for total mercury and methylmercury in the Plant.	4-21
Figure 4-19	Twenty-four hour sampling of influent to primary tanks	4-22
Figure 4-20	Total mercury and TSS concentrations at key Plant locations.	4-25
Figure 4-21	Flow and total mercury in Plant influent.	4-26
Figure 4-22	Flow and total mercury in Plant effluent.	4-27
Figure 4-23	Flow and methylmercury at the Plant influent.....	4-28

List of Tables

Table 3-1	Proposed Sampling Locations.....	3-4
Table 3-2	Mercury and Associated Water Quality Parameters.....	3-5
Table 3-3	Parameters and Laboratory Analytical Methods for SJ/SC Water Pollution Control Plant.....	3-6
Table 3-4	Sample Containers Used for Various Chemical Parameters.....	3-7
Table 3-5	Chemical Parameters and Preservatives and Holding Times	3-7
Table 4-1	Concentrations of mercury and methylmercury at various locations within the Water Pollution Control Plant	4-2
Table 4-2	Coefficient of variation of mercury at various locations within the Water Pollution Control Plant	4-3
Table 4-3	Average water and sludge flow volumes at various locations	4-19
Table 4-4	Long-term average mass balance at various Plant locations assuming average flow volumes at measured flow locations	4-20
Table 4-5	Total mercury load estimated for raw sewage, digester sludge, and final effluent.....	4-22
Table 4-6	Methyl-mercury load estimated for raw sewage, digester sludge, and final effluent.....	4-23
Table 4-7	Total mercury and methyl-mercury loads unaccounted when estimating a mass balance between raw sewage input and final effluent and digested sludge outputs	4-23
Table 4-8	Mann-Kendall trend analysis and seasonal trend analysis of mercury concentration versus time.	4-30

EXECUTIVE SUMMARY

The San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP or “Plant”) conducted a multi-year study of mercury fate and transport from October 2004 to May 2007. The study was focused on examining the efficiency and main mechanisms of mercury removal in various Plant processes and whether net production of more toxic forms of mercury (e.g. methylmercury) occurs in the Plant. Temporal variations in mercury concentrations under different flow conditions were also characterized. A mass balance of mercury in the Plant was developed to quantify losses of mercury through different pathways.

Sampling was conducted in two phases. Phase I was conducted from October of 2004 through September 2005. Grab samples were taken at various locations in the wastewater and sludge process streams. These samples were analyzed for total, dissolved and methylmercury using ultra-clean techniques. Wastewater samples were collected weekly at the following process locations: Raw Sewage (RS), Primary Effluent (PE), Settled Sewage (SS), Nitrification Effluent (NE), Secondary Effluent (SE), Tertiary Filter Influent (FI), Tertiary Filter Effluent (TFE), and Final Effluent (FE). Sludge samples were collected from Primary Sludge (PS), Nitrification - Waste Nitrification Sludge (WNS), Secondary - Waste Activated Sludge (WAS), Thickened Activated Sludge (TAS), Digester Sludge (DS), and Lagoon Sludge (SL) sources. More intensive sampling (4 hr interval in 24 hours) was also conducted for three sampling dates to characterize the diel pattern of mercury concentrations. Sampling was also conducted at the Biological Nutrient Removal (BNR) units to examine the potential production of methylmercury given the anaerobic conditions in the BNR units. Phase II sampling continued weekly to May 2007. This second phase was designed to examine longer-term seasonal trends and collect additional data for parameters where Phase I data found high variability. During phase II, RS and FE were sampled weekly, additional DS samples were collected, and BNR units were sampled at five locations in each of the two parallel BNR treatment trains.

The study showed that the Plant is highly efficient at removing mercury. Concentrations are reduced nearly 99%, 97%, and 50% for total mercury, methylmercury, and dissolved mercury, respectively. Influent loads of total mercury in raw sewage average 112 g/day (or 40.9 kg/yr), while the final effluent loads of total mercury average 0.97 g/day (or 0.35 kg/yr). Mercury removal at various process stages is closely related to total suspended solids (TSS) removal. Therefore, removal with solids was identified as the main mechanism for mercury

removal in the Plant. With the efficient removal of particulate associated mercury and methylmercury, dissolved mercury becomes the dominant form remaining in plant effluent. Average concentrations of total, dissolved and methylmercury concentrations in the plant effluent are at 1.9 ng/l, 1.4 ng/l and 0.04 ng/l, respectively.

Mercury concentrations in raw sewage show large temporal variation (coefficient of variation of 0.57 for total mercury). This variation is not associated with flow or season, although some peaks in concentrations were observed during high flow season. Mercury concentrations in the influent are correlated with TSS. The 24-hour intensive sampling indicates elevated total mercury concentrations between 2 pm and 10 pm. This indicates grab samples taken in the morning may be systematically biased low. This conclusion is supported by a comparison of morning grab sample data with twenty four-hour composite sample data from a parallel study; the raw sewage composite mercury concentrations are always higher than the morning grab sample values.

There was no evidence of net production of methylmercury, i.e., the Plant does not add to the toxicity or bioavailability of the mercury flowing through it. Methylmercury concentrations decrease along the process units (quads) in BNR. For the anaerobic sludge digesters, occasional increases in methylmercury concentrations relative to inflow were observed, indicating possible in-situ methylation. Limited data for the sludge were available to construct a full mass balance within the plant. The mass balance of mercury developed based on available data indicated that the majority of the total mercury is recovered in the digested sludge. Only 36 ± 10 % of the inflow methylmercury is recovered in sludge, with the remainder most probably lost through degradation. The most significant loss of methylmercury occurred in the BNR process.

The current effluent mercury load of 0.35 kg/yr is well below the allocated TMDL of 1 kg/yr. However additional improvement may be achieved through enhancing adsorption of dissolved mercury to the particles through oxidation to reduce complexation of dissolved mercury with ligands. Dissolved mercury was also found to increase after the filter backwash processes. Since the current mercury load is well within permit limits and targets for the San Francisco Bay Mercury TMDL, no process modifications specifically targeted toward further mercury reduction are currently planned. However, projects to enhance wet weather reliability are currently under way that will have the effect of reducing the likelihood of increased mercury releases under conditions of extraordinarily high flow. Continued improvements to efficiency at the Plant may also have beneficial mercury removal effects.

1.0 INTRODUCTION

This document presents the findings of a detailed multi-year study of mercury fate and transport within the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP or “Plant”) from October 2004 to May 2007. This study is required by the NPDES discharge permit for the Plant. The main objective of the study (as outlined in Chapter 2) is to better characterize the fate and transport of mercury in the Plant, specifically the variations in mercury concentrations under different flow conditions, the mechanisms of mercury removal in different processes, and whether transformation of mercury to more toxic forms (e.g. methylmercury) occurs in the Plant. A mass balance of mercury in the Plant was developed to quantify the losses of mercury through different pathways.

The San Jose/Santa Clara Water Pollution Control Plant (Plant) is one of the largest advanced wastewater treatment facilities in the United States. The Plant is located near Alviso, at the southernmost tip of the San Francisco Bay (Figure 1-1). The Plant treats the wastewater of over 1.3 million people that live and work in the 300-square mile area encompassing San Jose and surrounding communities. Most of the treated water from the Plant is discharged as fresh water through Artesian Slough into South San Francisco Bay. About 10% of the effluent is recycled and used for agricultural, landscaping, and industrial needs around the South Bay.

Elevated concentrations of mercury in fish and wildlife in the San Francisco Bay-Delta region have led to a US EPA 303(d) Impaired Water Body Listing for this system. In the wasteload allocation for the mercury TMDL for San Francisco Bay, all wastewater dischargers have been allocated a combined load of 17 kg per year, with the San Jose/Santa Clara Water Pollution Control Plant being allocated 1 kg/year. Currently the Plant discharges about 0.4 kg/year of mercury. The total allocated mercury load from all sources is 706 kg/year (from the September, 2004, Proposed Basin Plan Amendment prepared by the San Francisco Bay Regional Water Quality Control Board). Although there are many sources of mercury in the watershed of the San Francisco Bay Delta, wastewater mercury loads are important to consider because they have been suspected to be more bioavailable than other sources. In general, methylmercury is the most bioavailable form followed by dissolved Hg^{2+} compounds. Adsorbed mercury is less bioavailable. For the San Jose/Santa Clara Water Pollution Control Plant, an additional factor is that the discharge occurs in a portion of San Francisco Bay that receives much less fresh water runoff than the North Bay and experiences minimal advective flushing. During the dry parts of the year, the Plant’s discharge can comprise most of the South Bay’s fresh water inflow.

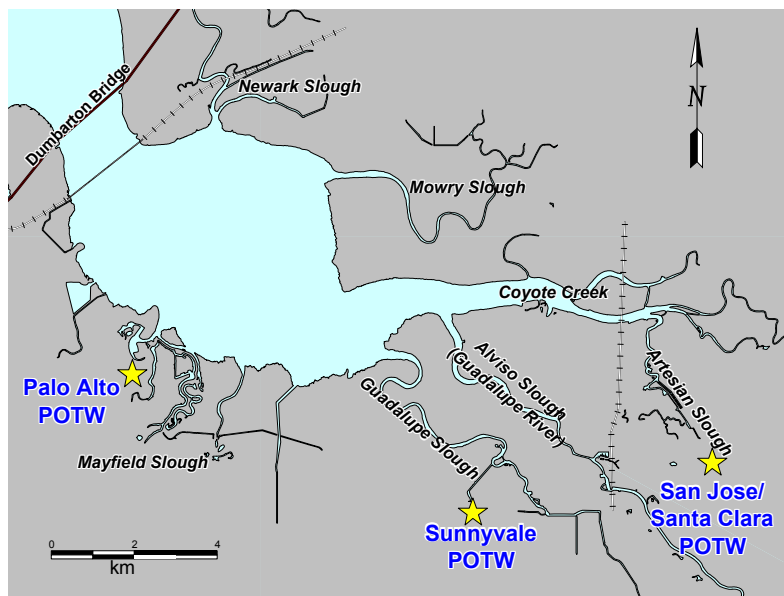


Figure 1-1 Location of San Jose/Santa Clara Water Pollution Control Plant and other major treatment plants in South San Francisco Bay.

Available monitoring data from the receiving waters of the Plant show that ambient mercury concentrations may be fairly high. Sampling conducted by the City of San Jose in Artesian Slough reported average values greater than 50 ng/l at the confluence of Artesian Slough and Coyote Creek (Watson et al., 1998). These high values may be caused by other upstream sources in Coyote Creek or by tidal influence from South San Francisco Bay. The total mercury at this location is consistent with other measurements in South San Francisco Bay using ultraclean techniques (Choe et al., 2003; Conaway et al., 2003) although most other stations sampled are likely to have been more strongly influenced by sources other than the Plant's flows.

1.1 MERCURY IN WASTEWATER TREATMENT PLANTS

A review of scientific literature conducted for the City of San Jose (Hsu, 2004) evaluated available information on mercury in wastewater treatment plants. Only a small number of studies were found that used ultraclean collection and analytical methods. From these studies it was found that total mercury in raw sewage ranged from 100 to 4,000 ng/l. These values are substantially higher than those observed in clean or minimally impacted aquatic systems as shown in Figure 1-2. Residential and industrial sources are responsible for this mercury input. Eighty percent of the residential sources originate in wastes from humans with dental amalgams (Association of Metropolitan Sewage Agencies, 2000). On average, wastewater treatment plants report removal of about 85% of influent mercury. The resulting effluent concentrations are thus of the same order of magnitude as those observed in natural waters (Figure 1-2).

Methylmercury concentration data for wastewater plants are also limited (Hsu, 2004). One study reported that the sewage treatment process was able to remove 90% of the influent load, although the resulting concentration was sometimes greater than the receiving water concentration as shown in Figure 1-3. It has also been suggested that wastewater treatment may cause production of methylmercury (Bodaly et al., 1998, cited in Hsu, 2004).

The affinity of mercury for particles is thought to play an important role in the removal of mercury from wastewater. Affinity of mercury to particles is either through formation of Hg-sulfide minerals or through adsorption to particle surfaces. Mercury entering the Plant therefore is mostly associated with particles. A mass balance study for a wastewater treatment plant in Minnesota estimated that approximately 80% of mercury was removed during primary treatment and was collected in the sludge (Balogh and Liang, 1995). Another study of a wastewater treatment plant found a positive correlation between mercury and the concentration of suspended particles in the final discharge.

Although a large fraction of the total mercury can remain attached to particles, and thus be subject to removal during settling and filtration, a small fraction does remain in aqueous form, strongly complexed with various inorganic or organic ligands present in wastewater. These aqueous forms may be more difficult to remove from the wastewater stream. Potential ligands include those that contain reduced sulfur functional groups such as sulfides, polysulfides, and sulfur-organic ligands such as thiols (Hsu, 2004). Recent work has indicated that aqueous mercury in wastewater plant discharges exists as strongly bound complexes (Hsu et al. 2003).

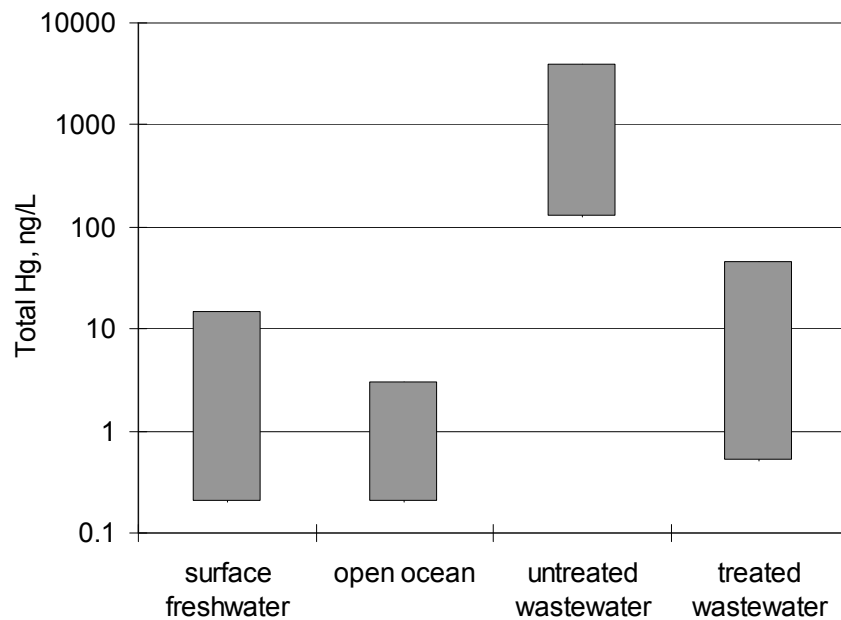


Figure 1-2 Range of total mercury concentrations in natural waters and untreated and treated wastewater. Source: Hsu, 2004

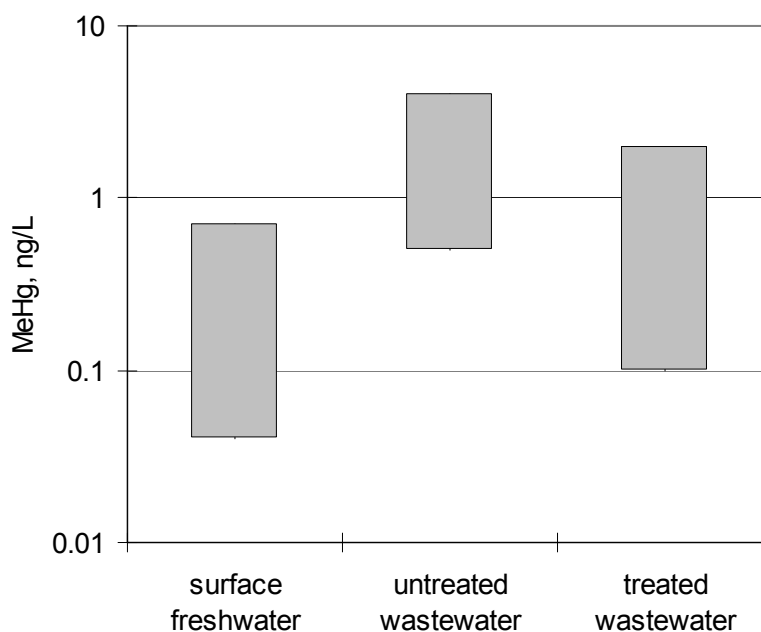


Figure 1-3 Range of methylmercury concentrations in surface waters and untreated and treated wastewater. Source: Hsu, 2004

Aside from wastewater-specific data, one may also infer potential mercury behavior within wastewater treatment plants from the large body of literature on mercury behavior in natural waters. It is well understood, for example, that transformation of inorganic mercury to methylmercury is mediated by bacteria that are most active under anoxic, sulfate-reducing conditions. Conversely, when sulfide concentrations are high, methylmercury production may be inhibited. Methylmercury production is expected to occur during anaerobic processes such as anaerobic sludge digestion. Likewise, bacterially-mediated reactions may convert methylmercury to less toxic forms. Reducing conditions may also convert inorganic mercury in the Hg^{2+} form to dissolved gaseous mercury that may volatilize. Reduction of Hg^{2+} to Hg^0 can occur both as biologically-mediated and abiotic redox processes. Reduction of Hg^{2+} by bacteria is via mercury reductase enzyme, which is most likely to occur in contaminated water with Hg^{2+} concentrations above 10 ng/l. Abiotic photochemical reduction of Hg^{2+} to Hg^0 may also occur in sunlit waters. However photochemical reduction is not expected to be a significant process in the wastewater treatment plant given the light attenuation by organic matter and high suspended solids. Oxidation of Hg^0 to Hg^{2+} may also occur through biotic and abiotic processes. Degradation of methylmercury can occur through a photochemical mechanism and two biologically-mediated pathways: through an enzyme that cleaves methylmercury to form CH_4 and Hg^{2+} and through oxidation demethylation to CO_2 (Hsu, 2004). Both of these biological demethylation processes can be carried out by aerobic and anaerobic bacteria.

Because of the range of aquatic chemistry conditions that arise during wastewater treatment, transformations of mercury to more toxic or mobile forms are plausible. Figure 1-4 shows the typical reactions of mercury and the potential for these reactions to be significant during wastewater treatment. However, the complexity of wastewater and mercury chemistry

precluded a predictive approach to explain mercury behavior inside wastewater treatment plants and called for process-specific data collection.

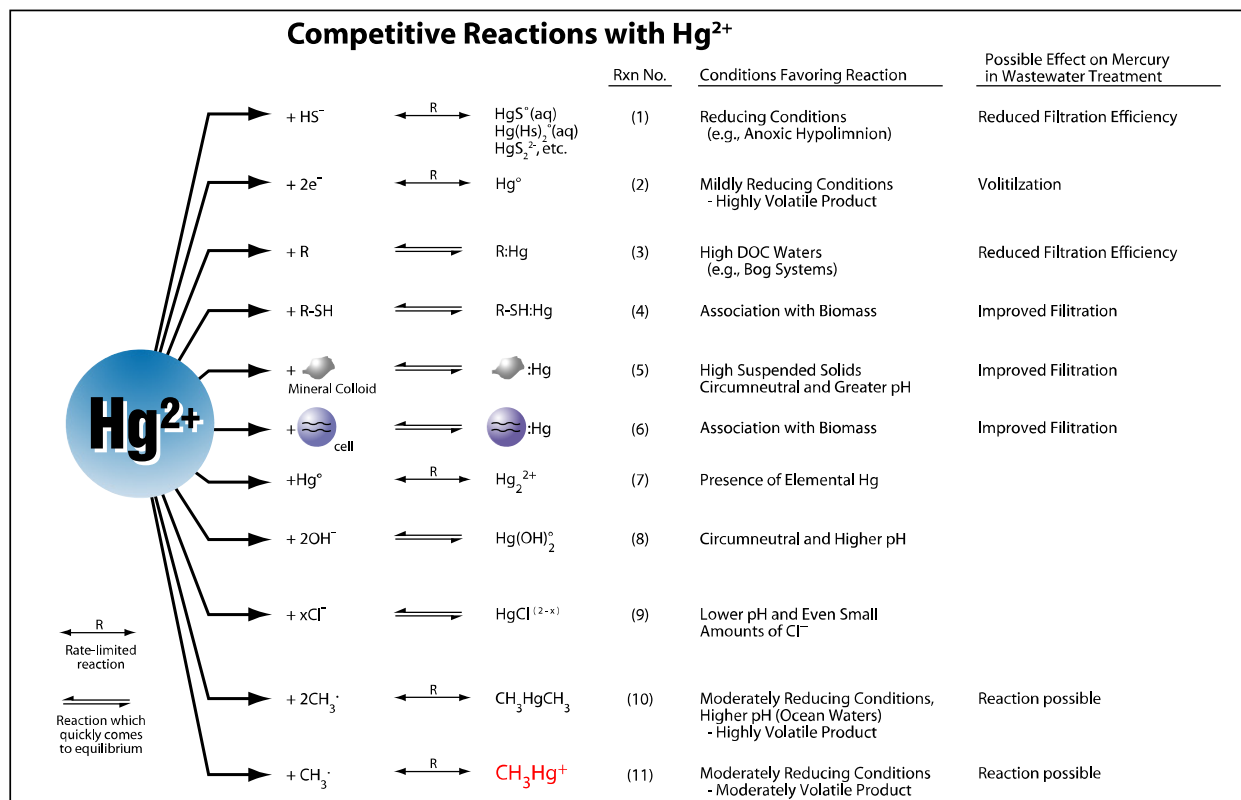


Figure 1-4 Mercury reactions in aquatic systems with emphasis on reactions that may effect wastewater treatment

1.2 OVERVIEW OF PLANT OPERATION

The San Jose/Santa Clara Water Pollution Control Plant is an advanced treatment plant that consists of screening and grit removal, primary sedimentation, secondary treatment (biological nutrient removal or BNR), secondary clarification, filtration, disinfection, and dechlorination before water is discharged into the environment. A simplified schematic of the plant is shown in Figure 1-5. Raw sewage first flows through screens for grit removal and then enters the primary settling tanks. The primary settling tanks have residence times of a little less than 2 hours, and settle out some of the particulate load carried by the sewage. The supernatant from these tanks, called the primary effluent, is then pumped into activated sludge biological nutrient removal (BNR) treatment. There are parallel BNR areas, which are identical in function, although, for historical reasons are called “Secondary” and “Nitrification” at the Plant. Each side is subdivided into banks of four compartments in series, where the flow travels from an anaerobic compartment, to an aerobic, anoxic, and finally an aerobic compartment (Figure 1-6).

Primary effluent (PE) and Return Activated Sludge (RAS) are pumped directly into the first compartment, which is maintained under anaerobic conditions (Figure 1-6). The second compartment is maintained under aerobic conditions with dissolved oxygen levels of 2-2.5 mg/L. This compartment is responsible for removal of readily degradable chemical oxygen demand (COD) and phosphorus, and for the conversion of ammonia to nitrite and nitrate.

The third compartment is anoxic and is used for conversion of nitrite and nitrate to nitrogen gas. Here the anoxic term is used specifically for the wastewater treatment process that converts nitrate to nitrogen gas (i.e. de-nitrification). DO levels in this compartment may not be significantly different from the anaerobic first compartment. A fraction of the primary effluent is pumped directly into this compartment to provide a source of BOD for oxidation. The final, aerobic, compartment is used to oxidize residual ammonia from the second and third compartments. Dissolved oxygen in this compartment is maintained at 4-4.5 mg/l. The total residence time in the activated sludge process is 4-5 hours. Water from the process is pumped into clarifiers to settle out the solids. The sludge stream from this process is sent for thickening via dissolved air flotation, followed by anaerobic digestion (with a residence time of 35 to 45 days) and delivery to sludge lagoons and solar drying ponds. Water from the clarifiers is then pumped through tertiary filters for additional solids removal. After filtration, the water is chlorinated for disinfection, and then dechlorinated using sulfur dioxide before discharge to the environment.

The physical separation processes and biochemical reactions in wastewater treatment are all expected to have an impact on mercury behavior. Prior to initiation of this study, it was known that the Plant was very efficient at removing total mercury. However, no information was available on (i) the fate of particular mercury species (such as dissolved mercury, gaseous mercury, and methylmercury), (ii) the different conditions that occur within the activated sludge treatment process, and (iii) the concentrations of mercury species in the sludge streams exiting the plant.

Inflows to the wastewater plant vary over the course of a day, and over different seasons in a year. The Plant has the capacity to treat 167 million gallons of wastewater per day (mgd), although in recent years average daily flows have been 120 mgd, ranging from about 95 to 160 mgd. Figure 1-7 shows the influent volume to Primary and the volumes being treated on the "Nitrification" and "Secondary" process paths. Most of the Plant effluent is discharged via the outfall, with a small fraction in the summer months diverted for various recycling projects (Figure 1-8).

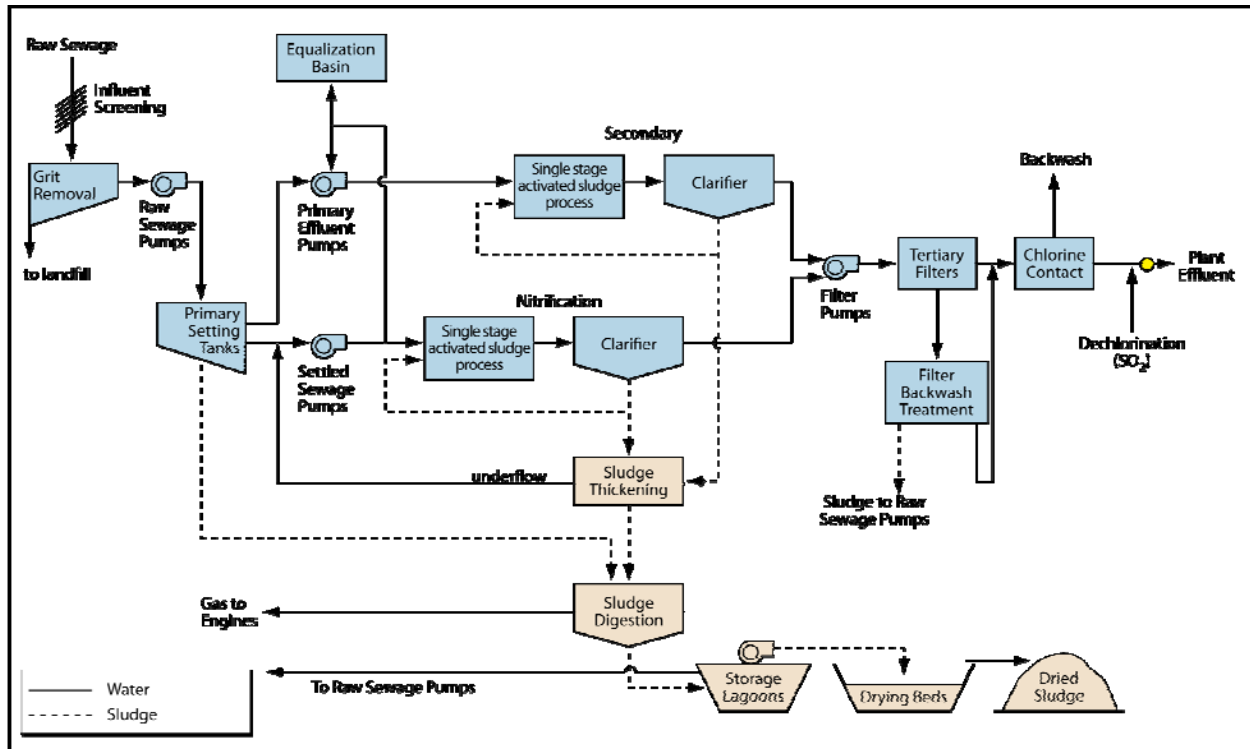


Figure 1-5 Simplified process diagram of San Jose/Santa Clara Water Pollution Control Plant. An important feature is the presence of parallel single stage activated sludge treatment units that are labeled “Secondary” and “Nitrification” processes for historical reasons. The influent and the treatment within the process is the same for both parallel paths. However, the quantity of flow handled by them may vary over the year. In summer, the “Secondary” side handles 80% of the flow with “Nitrification” handling 20% of the flow. In winter, when the flows are higher, the “Secondary” side handles 60% of the flow with “Nitrification” handling 40%.

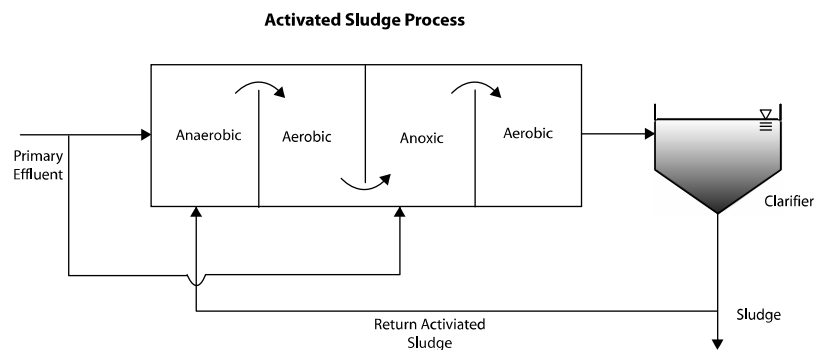


Figure 1-6 Schematic of single stage activated sludge processing basin, showing four quads that are maintained at different redox conditions.

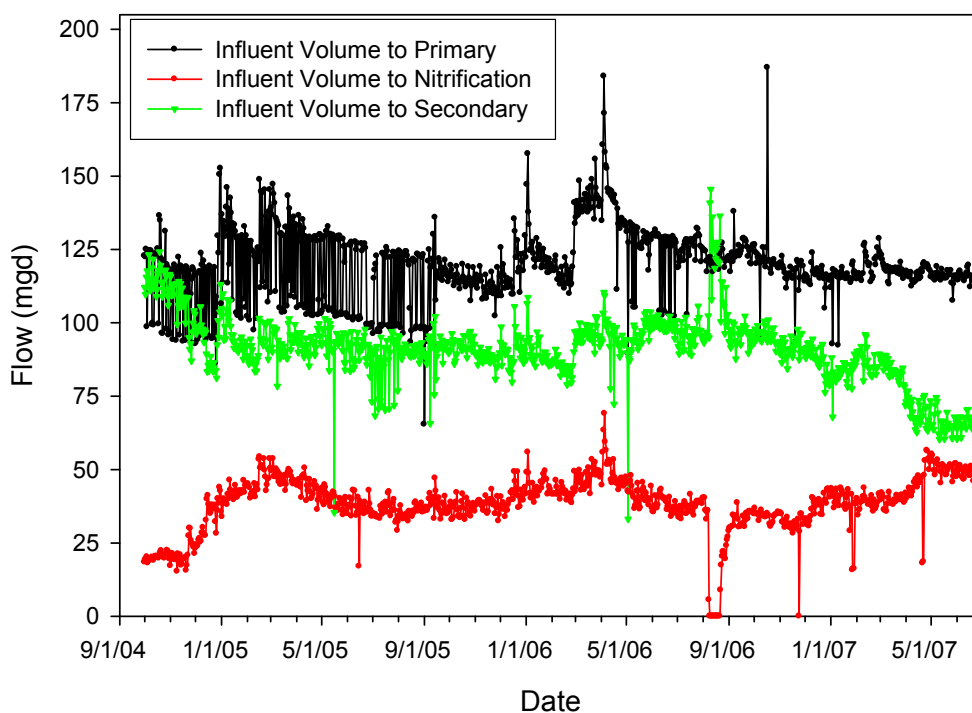


Figure 1-7 Daily average influent flow to Primary and volumes treated in the “Nitrification” and “Secondary” process paths.

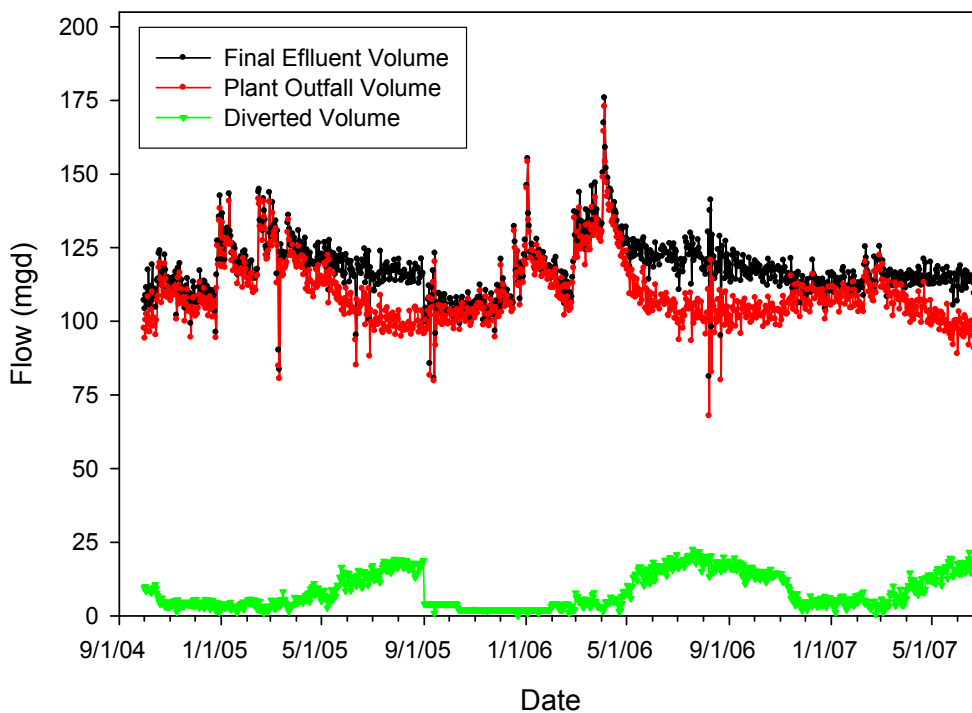


Figure 1-8 Daily average effluent flow (to the Plant outfall in Artesian Slough and diverted to recycled water pipelines).

1.3 REPORT ORGANIZATION

This report is divided into five chapters. Chapter 2 describes in more detail the objectives and the rationale for mercury sampling within the Plant. Chapter 3 provides information on sampling locations, collection and analysis methods, and sampling frequency. Chapter 4 presents results of mercury and ancillary data analysis, including mass balance analyses, analyses of concentration fluctuations of mercury through each treatment stage, and a review and discussion of potentially correlated parameters. Chapter 5 highlights key conclusions, provides recommendations, and identifies the major lessons learned from this exercise.

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2.0 SAMPLING OBJECTIVES

In an effort to better understand the nature of mercury contributions from wastewater treatment into San Francisco Bay, the Regional Water Board identified key sampling objectives outlined in a July 2004 letter to the City of San Jose:

- Understand the mechanisms of mercury removal in different process operations in the Plant
- Characterize the concentration and form of mercury at various locations in the Plant under a range of representative operating conditions
- Develop a mass-balance for the Plant to identify critical stages in the process and sinks for mercury
- Develop a two-phased approach to data collection, with a screening phase, and a second phase for more detailed analysis of specific components.

In-plant, individual process level, mercury sampling of this kind has not previously been reported for any wastewater treatment plant. This chapter presents the approach taken to meet each of the above objectives, including potential methods for increasing the effectiveness of future data collection and methods for analysis of data to be collected. Details of sampling locations, analysis methods, and sampling frequency are presented in Chapter 3.

2.1 UNDERSTAND THE MECHANISMS OF MERCURY REMOVAL IN DIFFERENT PROCESS OPERATIONS

The sampling was designed to measure concentrations of different forms of mercury before and after all major biological and physical separation processes within the wastewater treatment plant. The major process steps sampled include the raw sewage flow, the primary treatment, biological nutrient removal, anaerobic sludge digestion, filtration, disinfection, and the sludge stabilization ponds. In addition to mercury concentrations, several ancillary water chemistry parameters (such as total suspended solids, sulfate, sulfide, pH, chloride, and dissolved oxygen) were measured at the same time. As shown in Figure 1-4, these parameters are associated with mercury transformations that may occur in the treatment process, with potential for affecting the speciation and removal efficiency of mercury.

To estimate the mass balance of mercury in the Plant, specific points in the treatment process were identified and mass loads calculated. Because loads are a product of concentration and flow rate, flow data were obtained at selected locations where chemistry data were collected.

2.2 CHARACTERIZE THE CONCENTRATION AND FORM OF MERCURY AT VARIOUS LOCATIONS UNDER A RANGE OF REPRESENTATIVE OPERATING CONDITIONS

Total, dissolved and methylmercury were measured at each sampling event. These measurements allowed an examination of the potential for transformation of mercury from one form to another. Examples of potential transformations include: methylation of mercury in anoxic basins, the demethylation of mercury in secondary clarifiers, the settling of particulate mercury in primary settling basins and secondary clarifiers, and enhanced dissolution through aqueous complexes in the activated sludge process.

Measurements were made over a long time period to capture the broadest range of operating conditions through dry and wet-weather conditions. Wastewater treatment is a highly dynamic process with flows varying over the course of a day and over seasons. It is quite possible that mercury behavior, as well as the behavior of ancillary parameters, changes with operating condition. For example, mercury concentrations and removal efficiency in the Plant may exhibit seasonal variation, or the efficiency of filtration may be reduced during unusually high flow events.

An important objective of this study was to develop an understanding of the causes behind the variability in mercury concentrations through the Plant. More temporally intensive sampling was conducted at selected locations with flow, mercury concentration and ancillary water chemistry being monitored every four hours. Because this sampling is labor and cost intensive, this was accomplished at selected locations over three 24-hour periods, representing a range of weather conditions.

2.3 DEVELOP A MASS-BALANCE FOR MERCURY

Mass flows of mercury through key Plant locations were calculated over the time period of the sampling. Using flow and concentration data, estimates of mass balance of mercury were made to document the removal efficiency and net sinks for mercury. Because of potential variability of mercury concentrations at short time scales, the mass balance calculations were integrated over an extended time period to be meaningful.

2.4 TWO-PHASED APPROACH FOR DATA COLLECTION

The sampling described in this report consisted of two phases for understanding mercury behavior in the San Jose/Santa Clara Water Pollution Control Plant. During the first phase, temporally and spatially detailed sampling was performed to characterize mercury fate and transport including potential relationships with flow and ancillary water chemistry parameters. The second phase of the study built on results from the first phase to look at specific process steps in greater detail and to examine potential longer-term (seasonal) trends. Specific questions to be answered during the study included the following:

1. Can the variability in influent mercury in the plant be correlated with other factors (such as flow, season, etc.)?

2. What is the sample measurement variability, especially of particle-associated mercury species? Is the inflow concentration variability swamped by sample measurement variability?
3. Do the unique conditions that occur in wastewater treatment, notably anoxic conditions during activated sludge treatment, affect the methylation of mercury?
4. Are mercury concentrations related to other measurable water chemistry parameters in the treatment process (e.g., suspended particles, sulfide concentrations, etc.)?
5. Is the total mercury removal from the raw sewage concentrated in the sludge or is some of it lost to volatilization?
6. Which process steps are most effective at removing the different forms of mercury from the wastewater, and through what mechanism?
7. How variable is the mercury removal by individual treatment process steps for daily and seasonal changes in flow?
8. Where parallel treatment paths exist, do they behave similarly with respect to mercury removal?
9. How accurately can mass balances be determined for the plant as a whole, and for individual processes, given the inherent variability and measurement error in flow and concentrations?

3.0 SAMPLING LOCATIONS AND ANALYSIS METHODS

Mercury sampling for the San Jose/Santa Clara Water Pollution Control Plant included collection of wastewater and sludge samples at different points throughout the treatment plant. This chapter describes the sampling locations, parameters measured, sample collection methods, and analytical methods used.

3.1 SAMPLING LOCATIONS AND FREQUENCY

A recent Plant process diagram was used to identify the locations for mercury sampling. Composite and grab samplers are identified with the C and G symbols. Flow meters are identified with the F symbol (Figure 3-1). As discussed in Chapter 1, “Secondary” and “Nitrification” pathways shown in the process diagram are identical in function (biological nutrient removal or BNR) and receive the same influent (although the relative flow volumes may differ with season).

Sample locations were selected to provide estimates of mercury entering and leaving the Plant in aqueous and solid phases, and at intermediate points to quantify mercury fluxes within the various treatment processes within the Plant. The rationale underlying the choice of each of these stations is described in Table 3-1. Flow or level settings were used to supplement the existing flow data collected at the Plant. Estimates of sludge flows in the various units were made using volume measurements provided by Plant staff.

Sampling at the locations listed in Table 3-1 was conducted to estimate the variability in mercury concentrations and to identify the factors that are correlated with mercury concentration. The base level of sampling consisted of once-weekly samples at all locations with additional, intensive sampling conducted at selected locations. The intensive sampling was conducted over a 24-hour period on three occasions representing conditions of dry, intermediate and wet weather flow conditions. Mercury species concentrations and ancillary parameters were measured every four hours during each 24-hour sampling period. The intensive sampling locations were: raw sewage (RS), primary effluent (PE), “Nitrification” effluent (NE), “Secondary” effluent (SE), tertiary filter influent (FI), tertiary filter effluent (TFE), and final effluent (FE).

In Phase 2, weekly sampling was scaled back to RS and FE, and the entire suite of locations sampled monthly. Special attention was also given to the BNR Quad tanks and Digester Sludge during this phase. Five samples from each of the two parallel BNR treatment streams representing the inlet to the first quad tank and the end of each quad tank were taken once per week for ten consecutive weeks from 3/7/2007 to 5/9/2007. Fifteen additional digester sludge (DS) samples were also taken from 4/19/2007 through 6/8/2007 to better estimate the mercury and methylmercury exported.

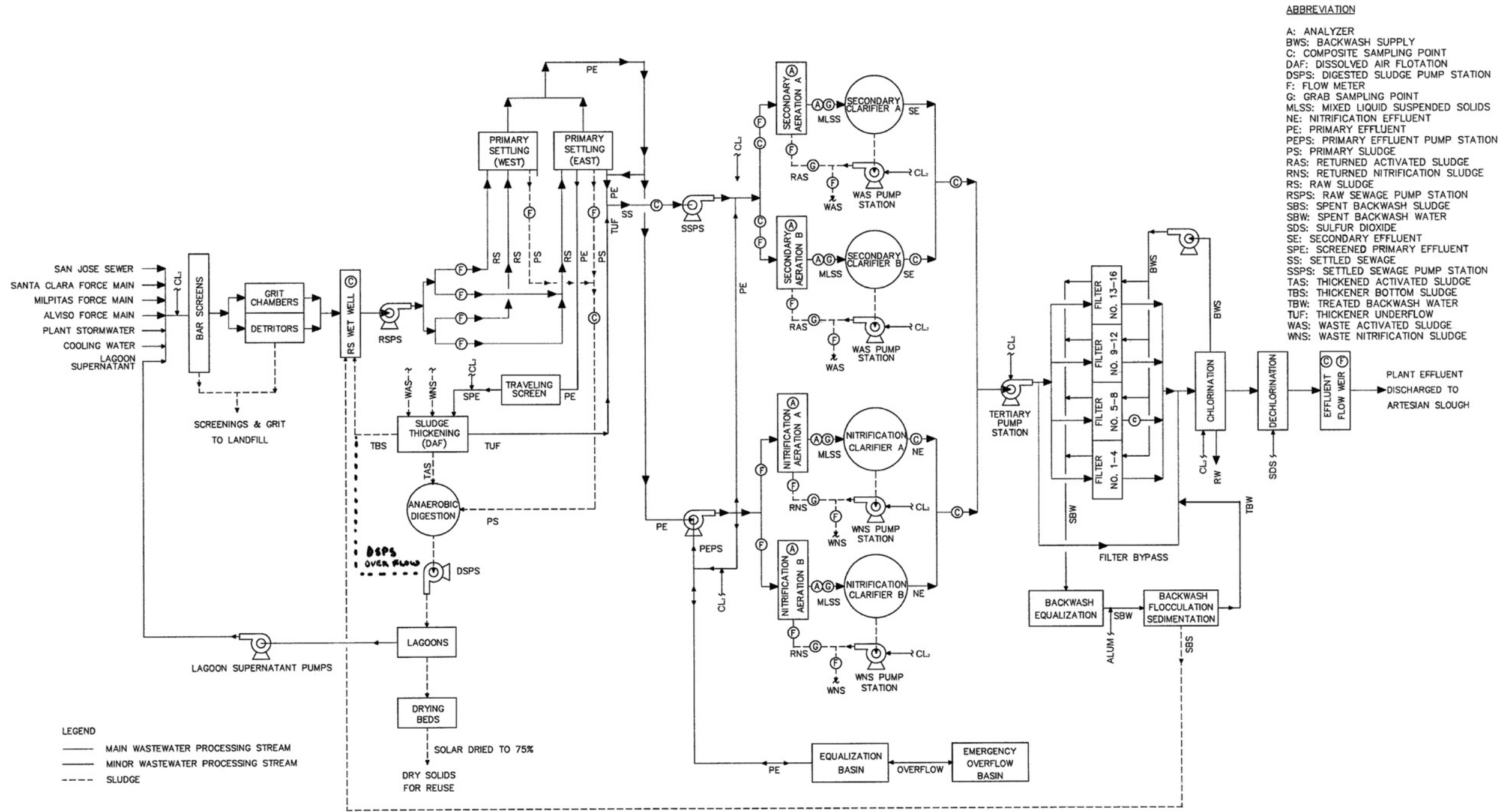


Figure 3-1 Process flow diagram for San Jose/Santa Clara Water Pollution Control Plant with sampling locations identified

**Table 3-1
Proposed Sampling Locations**

Sample ID	Location	Media	Rationale for Sampling	Intensive 24-hour Sampling
RS	Raw Sewage from Pumps to Primary Settling Tanks	Wastewater	Characterize raw sewage influent	Yes
PE	Primary Effluent	Wastewater	Characterize changes in composition after primary settling	Yes
SS	Settled Sewage Influent to Nitrification Units	Wastewater	Characterize influent and compare to detailed unit sampling	
NQ1 through NQ4	Output from Nitrification Quad Units 1-4	Wastewater	Characterize changes in nitrification unit processes	
NE	Nitrification Effluent	Wastewater	Characterize changes after nitrification units and clarifier	
SQ1 through SQ4	Output from Secondary Units (also Nitrification)	Wastewater	Characterize changes in nitrification unit processes	
SE	Effluent from Secondary Units and clarifier	Wastewater	Characterize changes after secondary units and clarifier	
FI	Tertiary Filter Influent	Wastewater	Characterize influent to series of filters (4 sets of 4 units)	Yes
FBW	Treated Filter Backwash	Wastewater	Characterize effluent from filter backwash treatment added back before chlorine contact	
TFE	Tertiary Filter Effluent	Wastewater	Characterize changes after tertiary filters	Yes
FE	Final Sewage Effluent	Wastewater	Characterize final effluent after chlorination – dechlorination	Yes
PS	Primary Sludge	Sludge	Characterize sludge from primary settling basins	
WAS	Waste Activated Sludge from Secondary Units	Sludge	Characterize sludge from secondary aeration & clarifier units	
RAS	Returned Activated Sludge	Sludge	Characterize returned sludge from secondary clarifiers	
RNS	Returned Nitrification Sludge	Sludge	Characterize returned sludge from nitrification clarifier units	
WNS	Waste Nitrification Sludge	Sludge	Characterize sludge from nitrification & clarifier units	
TAS	Thickened Activated Sludge	Sludge	Characterize changes in solids after sludge thickening unit	
DS	Digested Sludge	Sludge	Characterize changes in sludge after digestion	

3.2 PARAMETERS AND ANALYTICAL METHODS FOR WASTEWATER, SLUDGE, AND AIR SAMPLES

Wastewater samples were collected using ultra-clean techniques and analyzed for four forms of mercury (total and filtered mercury, filtered and unfiltered methylmercury). Other ancillary parameters measured in wastewater samples included total suspended solids, chloride, sulfate, and sulfide. Measurements of dissolved oxygen (DO), pH, temperature, specific conductance, and turbidity were made at the time of sample collection. The rationale for conducting each of the chemical measurements is presented in Table 3-2. Laboratory methods for these parameters are listed in Table 3-3. The laboratory analytical methods were selected to provide the required precision, accuracy, and detection limits necessary to meet the objectives of the

project. Details of analytical methods used in this project are summarized in a separate Sampling and Analysis Plan (submitted by the City of San Jose to the San Francisco Bay Regional Water Quality Control Board in September 2004).

Table 3-2
Mercury and Associated Water Quality Parameters

Parameter	Importance to Mercury Behavior
Mercury Measurements	
Total Unfiltered Mercury	Used for water column mercury load calculations.
Filtered Mercury	Filtered mercury is considered dissolved although Hg can still be highly complexed or associated with colloids. Dissolved Hg is considered more bioavailable than total mercury.
Unfiltered Methylmercury	Includes dissolved and particulate forms, less bioavailable than filtered methylmercury.
Filtered Methylmercury	Dissolved methylmercury, which is more bioavailable than methylmercury associated with particulates
Ancillary Measurements	
Dissolved Oxygen (DO)	Mercury methylation occurs under anoxic conditions, where DO drops below about 1-2 ppm. Demethylation favored at higher DO values.
pH	Demethylation reactions and Hg off-gassing favored by slightly alkaline pH values (above 7). Hg^{2+} passage through cell membranes is thought to be favored by formation of $\text{Hg}(\text{OH})_2^0$ species.
Chloride	Complexes readily with Hg^{2+} , and is thought to facilitate Hg passage through cell membranes. At high Cl concentrations (e.g. estuaries) forms negatively-charged ions with Hg^{2+} that are less readily transported into cells, so less available for methylation.
Sulfate	Methylation of mercury is largely carried out cometabolically by sulfate-reducing bacteria. Low sulfate (<10 mg/L) can limit methylation rate. Effect at high concentrations thought to be less significant, but some researchers speculate that high sulfate above 40 mg/L inhibits methylation.
Sulfide	Presence at concentrations above about 30 μmoles implies strongly reducing conditions, low redox potential. Forms low solubility precipitates with Hg^{2+} .
Suspended Solids	Most mercury in natural waters is associated with and transported by suspended solids.

Table 3-3
Parameters and Laboratory Analytical Methods for SJ/SC Water Pollution Control Plant

Parameter	EPA Method No.	Units	Reporting Limit
Water			
Total Mercury	1631	ng/L	0.2 ng/L
Dissolved Mercury	1631	ng/L	0.2 ng/L
Methylmercury	1630	ng/L	0.05 ng/L *
Total Suspended Solids	160.2	mg/L	5 mg/L
Chloride	300	mg/L	1 mg/L
Sulfate	300	mg/L	1mg/L
Sulfide	376.1	mg/L	0.01 mg/L
Sludge Samples			
Total Mercury	1631	ng/g	0.5 ng/g
Methylmercury	1630	ng/g	0.2 ng/g
Sulfide	9030	mg/kg	0.5 mg/kg
Sulfate	300	mg/kg	10 mg/kg
pH	9045C	St pH units	St pH units
Moisture Content	ASTM D2216	% by wt	0.01% by wt

*Methylmercury concentrations between the MDL (0.01 ng/L) and RL (0.05 ng/L) will be provided as J-flagged values.

Parameters Measured in the Plant

Temperature, pH and dissolved oxygen will be measured at the time of sampling in the plant.

3.3 WATER SAMPLING PROCEDURES

Details of sampling procedures used in this work are presented in a separate Sampling and Analysis Plan (submitted by the City of San Jose to the San Francisco Bay Regional Water Quality Control Board in September 2004) and are summarized here for reference.

3.3.1 MERCURY WATER SAMPLING

Existing composite samplers at Plant collect samples for process monitoring. Samples from these devices were not used for the mercury analysis, because their 8-liter sample bottles are filled sequentially over a period of time, and there is remaining headspace in the sample bottle. Instead, grab samples were collected into Teflon and amber glass bottles as described below. Field personnel followed EPA Method 1669 sampling procedures and techniques (“clean hands-dirty hands” technique).

3.3.2 WATER SAMPLING FOR ANCILLARY WATER QUALITY PARAMETERS

At each location where mercury was analyzed, a separate sample bottle was filled for each parameter. All water sample bottles for ancillary parameters were completely filled with no head-space (the space between the surface of the sample and the cap). The type of container for each parameter is listed in Table 3-4. The containers for non-mercury parameters were pre-labeled, identifying sampling location and organized into coolers to provide a sample kit for each event. The holding times for each chemical parameter and preservatives, if required, are listed in Table 3-5.

Table 3-4
Sample Containers Used for Various Chemical Parameters

Container	Testing	Requirements
125 ml HDPE	Chloride, Sulfate, Sulfide	Clean Containers
1 Liter HDPE	Total Suspended Solids	Clean Containers
1 L PTFE for water	Dissolved Mercury, Methylmercury (filtered)	Ultra clean prep. (See SOPs for bottle washing and filtering in QAPP)
1 L Amber Glass for Water	Total (unfiltered) Mercury, Methylmercury	Ultra clean prep. (See SOPs for bottle washing in QAPP)
1 L Amber Glass	Total Mercury in Sludge	Ultra clean prep. (See SOPs for handling)
1 L Amber Glass	Methylmercury in Sludge	Ultra clean prep (See SOPs for handling in QAPP)
250 mL HDPE	Sulfate in Sludge	Clean Containers
250 mL HDPE	Sulfide in Sludge	Clean Containers

Table 3-5
Chemical Parameters and Preservatives and Holding Times

Matrix	Parameter	Preservative	Laboratory Preparation	Holding Time
Water	Total Hg	Cool to < 4 °C	Acidify in lab (0.4% HCl)	28 days after preservation
	Dissolved Mercury	Cool to < 4 °C	Filter for dissolved Hg then acidify	28 days after preservation
	Methylmercury	Hydrochloric acid (HCl)	Acidify in lab (0.4% HCl)	28 days after preservation
	Sulfate	Cool to < 4 °C	None	28 days
	Sulfide	Zinc Acetate & NaOH	None	7 days
	Chloride	Cool to < 4 °C	None	28 days
	TSS	Cool to < 4 °C	Separation	7 days
Sludge	Total Mercury	Cool to < 4 °C	See SOP in QAPP	28 days
	Methylmercury	Cool to < 4 °C	See SOP in QAPP	28 days
	Sulfate	Cool to < 4 °C	Digestion	6 months
	Sulfide	Cool to < 4 °C	Digestion	6 months
	Moisture Content	None	None	2 days for Hg samples

Water samples were collected using the following procedures:

- **Clean Techniques** – All aqueous mercury sample bottles were double bagged. Anion sample bottles were single bagged and TSS bottles were not bagged. Prior to collecting each sample, sample bottles were rinsed three times with sample water. The rinse procedure is as follows: (1) fill sample bottle with sample until it is approximately 10% filled, (2) close cap, (3) shake vigorously, (4) discard, (5) repeat two additional times, and (6) collect sample.
- **Preservation of samples** – During sample collection at the Plant, samples were kept on blue ice until they were turned in to the Laboratory. Following check-in, samples were preserved by maintaining them at $4 \pm 2^{\circ}\text{C}$ or by adding the appropriate chemical preservative (Table 3-5). Samples were held according to the standard

methods employed (Table 3-5). Samples were usually taken no more than 2 hours before preservation in the analytical laboratory which is located on site at the Plant.

- **Field Blanks** – A field blank was collected following all Plant sample collections by pumping reagent water through the sampling equipment (Teflon tubing) for two minutes following sample collection and then collecting a sample using clean techniques (i.e. 3 bottle rinses).

3.3.3 MEASUREMENT OF FIELD PARAMETERS

Handheld instruments were used to measure pH, temperature, dissolved oxygen, turbidity, and conductivity *in-situ* at each sampling location.

3.4 SLUDGE SAMPLING PROCEDURES

Sludge samples were collected for analysis of mercury and methylmercury using a new, pre-cleaned, disposable polyethylene scoop and placed into separate 500-mL Teflon bottles with air-tight-fitting Teflon-lined caps. A new scoop was used for each sampling location. Sludge water content was determined so that analytical results can be used in the mass balance calculations.

3.5 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES

Details of QA/QC procedures are summarized in a separate Sampling and Analysis Plan (submitted by the City of San Jose to the San Francisco Bay Regional Water Quality Control Board in September 2004).

4.0 RESULTS

This chapter presents data from the mercury fate and transport study in the San Jose/Santa Clara Water Pollution Control Plant. Information is presented on concentrations of key constituents through the wastewater treatment process, correlations between selected parameters, and mass balances of mercury in the plant from October 2004 to May 2007.

4.1 MERCURY SPECIES IN AQUEOUS PHASES

Average concentrations of the four forms of mercury analyzed in this study (total mercury, dissolved mercury, total and dissolved methylmercury) are shown in Table 4-1 for each of the locations sampled. The summary data represent weekly results from October 2004 to May 2007. Included in these averages are data from three sampling dates during which 6 samples were collected each day. Also, concentrations at some locations on certain dates are the average of two measurements. Dissolved methylmercury sampling at some process locations began in March 2005.

Total mercury concentrations decrease by nearly 99% from an average of 144.8 ng/l in raw sewage (RS) to an average of 1.9 ng/l in the final effluent (FE). Concentration decreases occur at various steps, but the largest percentage decrease occurs as a result of the activated sludge secondary process as indicated by the lower concentrations in “secondary” effluent (SE), “nitrification” effluent (NE) and filter influent (FI) (Table 4-1 and Figure 4-1). Filter influent is a combination of SE and NE. Because the range of concentrations is fairly large, box plots of the data are plotted using both linear and logarithmic scales to show the changes that occur in the final stages of the wastewater treatment¹. The total mercury removal is well-correlated with the removal of TSS through the plant as described in greater detail below. Total mercury numbers are highly variable, especially in the raw sewage (coefficient of variation of 0.57, Table 4-2). Concentrations and variability both decrease after the first two process steps during treatment. The average WPCP effluent total mercury concentration (1.9 ng/l) is near the low end of concentrations observed in wastewater treatment plants (0.5-50 ng/l, Hsu, 2004).

Dissolved mercury is a small fraction of the total mercury (less than 2%) and its concentrations are not reduced as efficiently as total mercury. Concentrations in the final

¹ All box plots presented in this chapter display data according to the following conventions. The lower and upper ends of the box represent the 25th and 75th percentiles of the data, the ends of the whiskers represent the 5th and 95th percentile, and the solid line through the box represents the median. Outliers are shown with symbols.

effluent are about 50% of the levels in raw sewage (1.4 ng/l compared to 2.7 ng/l). A substantial reduction of dissolved mercury occurs in the BNR secondary step (Table 4-1 and Figure 4-2). In fact there is a marginal increase in dissolved mercury levels between SE/NE and the final effluent (Table 4-1). Variability in dissolved mercury concentrations is low at the intermediate and later locations with the exception of filter backwash (FBW), and is higher at other locations (Table 4-2). Filter backwash is treated by flocculation and clarification, and the clarified product is added back to filter effluent before disinfection. This probably accounts for the slight increase in many constituents between filter effluent (TFE) and final effluent. Dissolved mercury also seems to increase from RS to primary effluent (PE), indicating possible dissolution of adsorbed mercury in the primary settling process. Due to the removal of particulate associated mercury, dissolved mercury accounts for a large percentage in the plant effluent (74%).

Methylmercury, which may exist in dissolved and particulate forms, constitutes a very small percentage of total mercury than dissolved mercury in the inflow to the Plant (about 1% in RS). During the treatment of wastewater through the Plant, there is a substantial reduction in methylmercury concentrations, from an average of 1.63 ng/l to 0.04 ng/l, a decrease of nearly 97% (Table 4-1 and Figure 4-3). Dissolved methylmercury accounts for a small percentage of the total methylmercury in RS (10.5%), and the dissolved fraction increases in the FE (75%) as methylmercury associated with particles is removed in the treatment processes. A key observation from these data is that there is no evidence of net mercury methylation in the Plant, especially at the SE/NE sludges, which are preceded by anoxic treatment conditions in the BNR secondary process (Figures 4-4 & 4-5 as discussed below).

Table 4-1
Concentrations of mercury and methylmercury at various locations within the Water Pollution Control Plant

Sample Location	Total Mercury Average (ng/l)	Dissolved Mercury Average (ng/l)	Methylmercury Average (ng/l)	Dissolved Methylmercury Average (ng/l)
RS—Raw Sewage	144.8	2.7	1.63	0.17
PE—Primary Effluent	87.6	3.8	1.51	-
SS—Settled Sewage	74.4	3.6	1.17	-
NE—Nitrification Effluent	4.5	1.0	0.05	0.02
SE—Secondary Effluent	5.2	1.1	0.04	0.03
FI—Filter Influent	5.0	1.1	0.05	-
TFE—Tertiary Filter Effluent	1.6	1.2	0.03	-
FBW—Filter Backwash	4.7	1.9	0.11	-
FE—Final Effluent	2.2	1.4	0.04	0.03

Table 4-2
Coefficient of variation (standard deviation divided by mean, CV) of mercury at various locations
within the Water Pollution Control Plant

Sample Location	Total Mercury CV	Dissolved Mercury CV	Methylmercury CV
RS—Raw Sewage	0.57	0.38	0.37
PE—Primary Effluent	0.45	0.36	0.48
SS—Settled Sewage	0.42	0.21	0.49
NE—Nitrification Effluent	0.39	0.15	0.39
SE—Secondary Effluent	0.35	0.15	0.31
FI—Filter Influent	0.26	0.19	0.30
TFE—Tertiary Filter Effluent	0.32	0.39	0.39
FBW—Filter Backwash	0.38	0.52	0.39
FE—Final Effluent	0.55	0.21	0.37

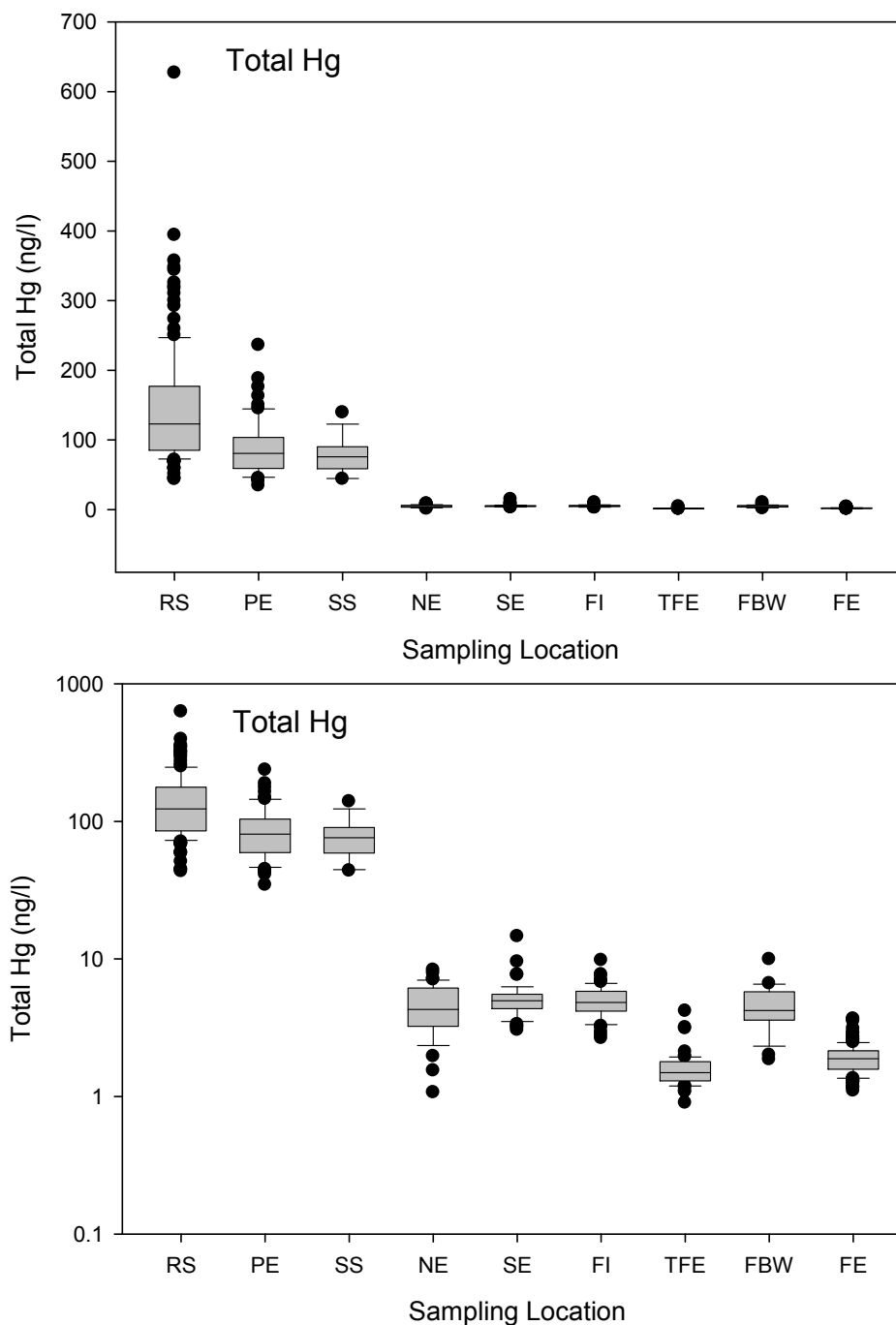


Figure 4-1 Total mercury in the San Jose/Santa Clara Water Pollution Control Plant. The lower panel shows the data in logarithmic scale to highlight the changes in all the process steps.

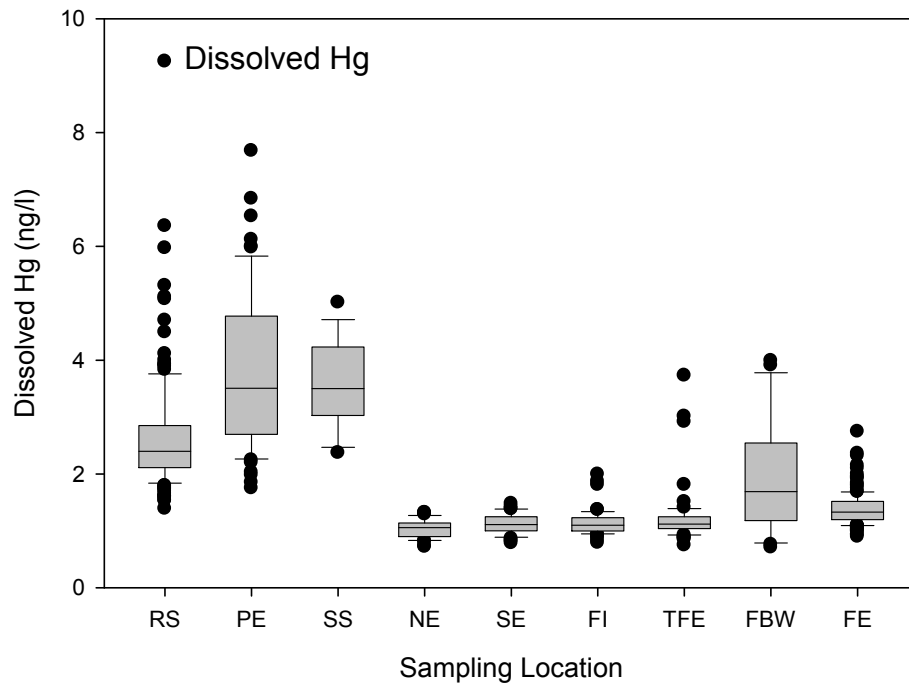


Figure 4-2 Dissolved mercury in different Plant process steps.

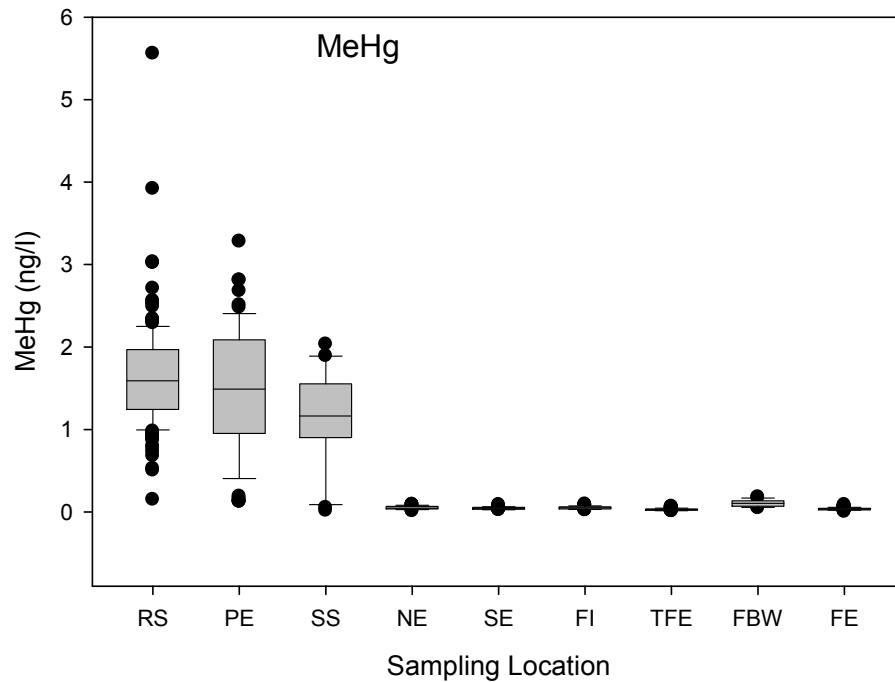


Figure 4-3 Total unfiltered methylmercury in different Plant process steps.

4.2 MERCURY SPECIES IN SLUDGE

Sludge samples at various locations were collected for total and methylmercury analysis. Sludge was sampled less frequently than the aqueous phase (total of four or five measurements were made during the study period). Sludge sampling locations included Primary Sludge (PS), Waste Activated Sludge from “Secondary” BNR pathway (WAS), Waste “Nitrification” BNR Sludge (WNS), Thickened Activated Sludge (TAS), Digested Sludge (DS), and Lagoon Sludge (SL).

Mercury concentrations in sludge are substantially higher than in the water stream. This was expected due to the strong particle association of mercury. Wet weight mercury concentrations in sludge were roughly twice in PS what they were in other sludges (Figure 4-4). Wet concentrations appear to be very similar in WAS, WNS, TAS and DS. The SL samples show large variation across the sampling dates. Total mercury concentrations in sludge on a dry basis show larger variations across the sampling dates. Similarly higher concentrations were observed in PS compared to WAS and WNS. Concentrations on a dry weight basis are elevated at the sludge thickening and digested sludge locations compared to other locations (Figure 4-4). Methylmercury shows more uniform concentrations through the wastewater treatment process on both dry and wet bases (Figure 4-5).

Methylmercury on a dry weight basis showed elevated concentrations in DS relative to the TAS and PS for 4 out of the 5 sampling dates. Total mercury concentrations also increase between TAS and DS. Methylmercury concentrations normalized to total mercury indicated there are slight increases in 2 of the 5 sampling dates. Therefore occasional methylation seems to occur in DS, however more sampling is needed to confirm the observation.

Additional sampling of mercury in DS during 04/07-06/07 indicated a slightly increasing trend during the warmer months. The four quads in the activated sludge process were sampled for total and methylmercury in both the “Nitrification” and “Secondary” paths during 10/2004-3/2005 and again on a weekly basis during 03/07-05/07. During 2007, sampling stations were modified to include the inlet to Quad 1 and the ends of all 4 quads to examine the effects of each individual quad on transformations of mercury. Of interest to mercury transformations, Quads 1 and 3 contain lower dissolved oxygen conditions that may favor methylmercury production, especially if there is potential for sulfate reduction. However, for both total and methylmercury, variation across sampling dates was greater than variation across quads (Figure 4-6 and 4-7). No clear pattern for total mercury was observed in quads of SE. Total mercury concentrations were higher in Quad 2 of the “Nitrification” side of the process. Methylmercury concentrations generally show a decreasing trend across the quads for both SE and NE. It appears that low dissolved oxygen portions of the activated sludge treatment process at the Plant do not have a measurable effect on net mercury methylation.

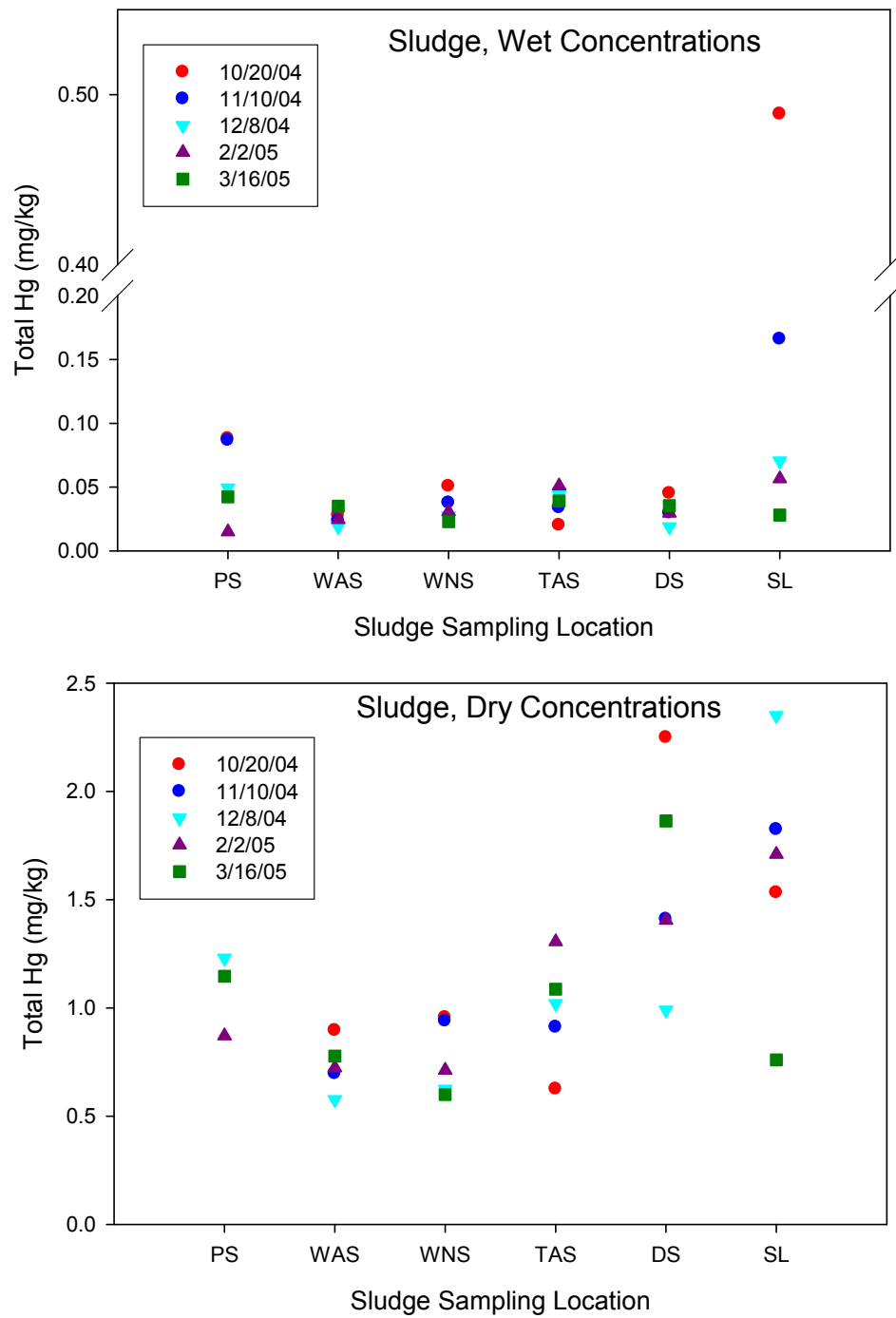


Figure 4-4 Mercury concentrations in sludge at different Plant locations.

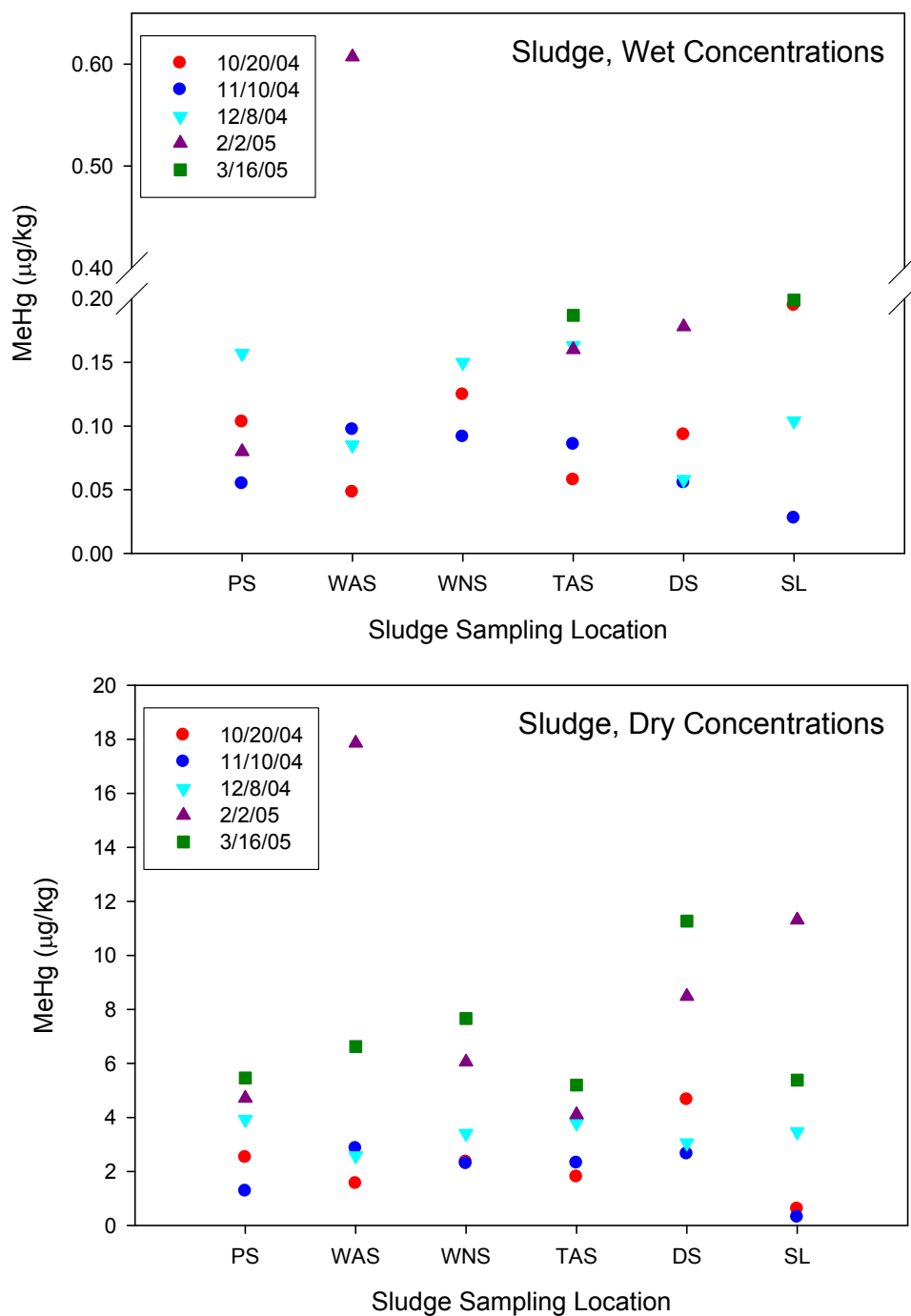


Figure 4-5 Methylmercury concentrations in sludge at different Plant locations.

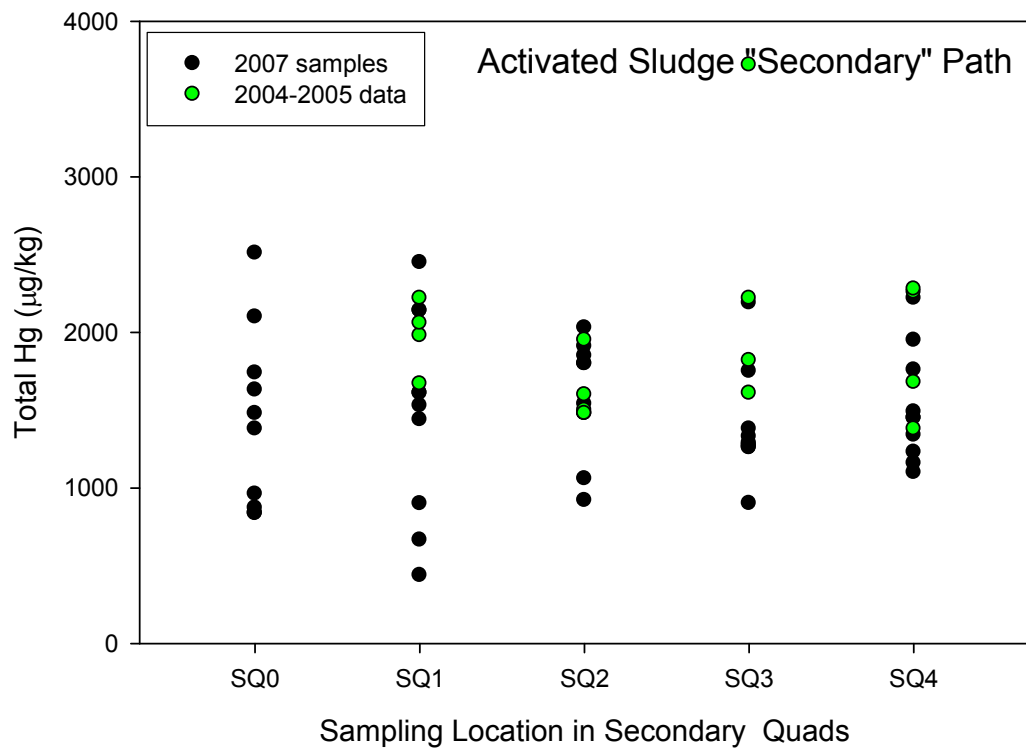
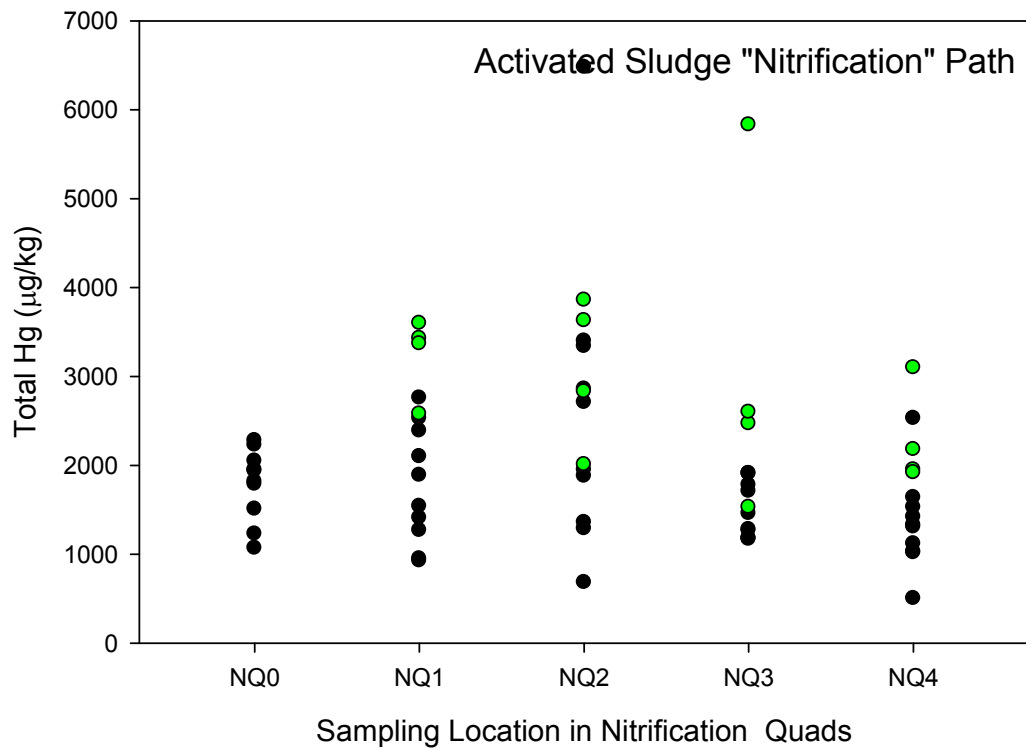


Figure 4-6 Total mercury concentrations in different quads of the activated sludge process. Quad 1 and QUAD 3 are anaerobic, Quad 2 and 4 are aerobic (shown in Figure 1-6). See discussion of the Plant process in Chapter 1.

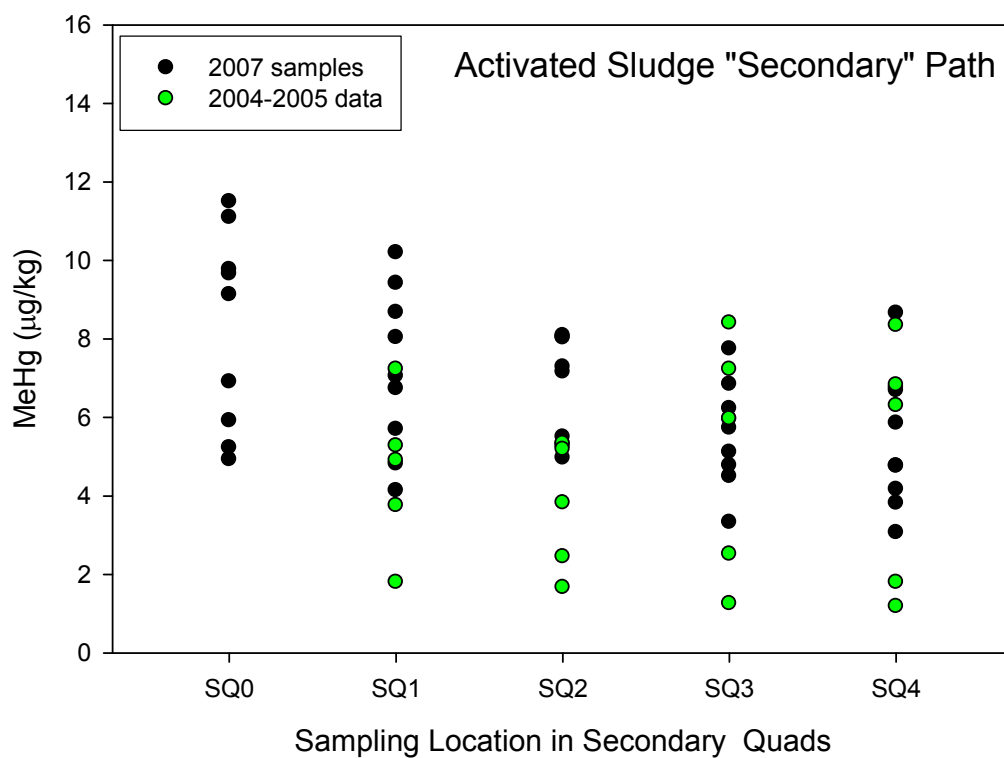
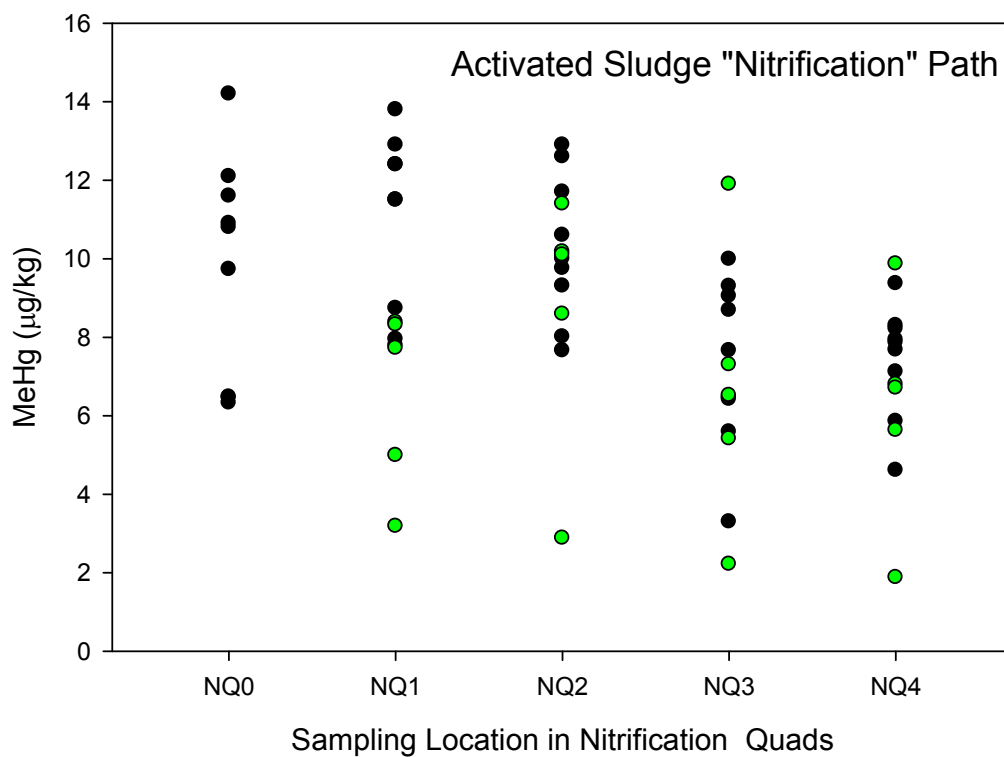


Figure 4-7 Methylmercury concentrations in different quads of the activated sludge process.

4.3 ANCILLARY PARAMETERS

Over the narrow range of conditions studied, on-site measurements of dissolved oxygen (DO) and pH are of interest in mercury transformation reactions. Dissolved oxygen in water samples increased through the treatment steps (Figure 4-8). Concentrations were lowest at PE and SS and increased in subsequent processes. Although the activated sludge process is expected to create anoxic conditions, these zones were not measured for this study, and effluents from these treatment steps (specifically SE and NE) were not anoxic. The pH levels across the different process steps varied over a narrow range (Figure 4-9). The small variation of pH is unlikely to influence mercury chemistry.

TSS concentrations showed the greatest change during treatment of any ancillary parameter monitored (Figure 4-10). Concentrations decreased from an influent average of nearly 200 mg/l to less than 2 mg/l. As discussed later, TSS concentrations are correlated with total mercury concentrations at several Plant locations.

Sulfide, sulfate, and chloride were also measured. Sulfide concentrations were largely not detected at most locations within the Plant and are not shown graphically (more than 90% of the samples were below the detection limit of 0.1 mg/l). Chloride and sulfate were both measured at roughly constant levels at all Plant locations (Figures 4-11 and 4-12). These constituents are relatively conservative during wastewater treatment and their relatively uniform levels are not surprising.

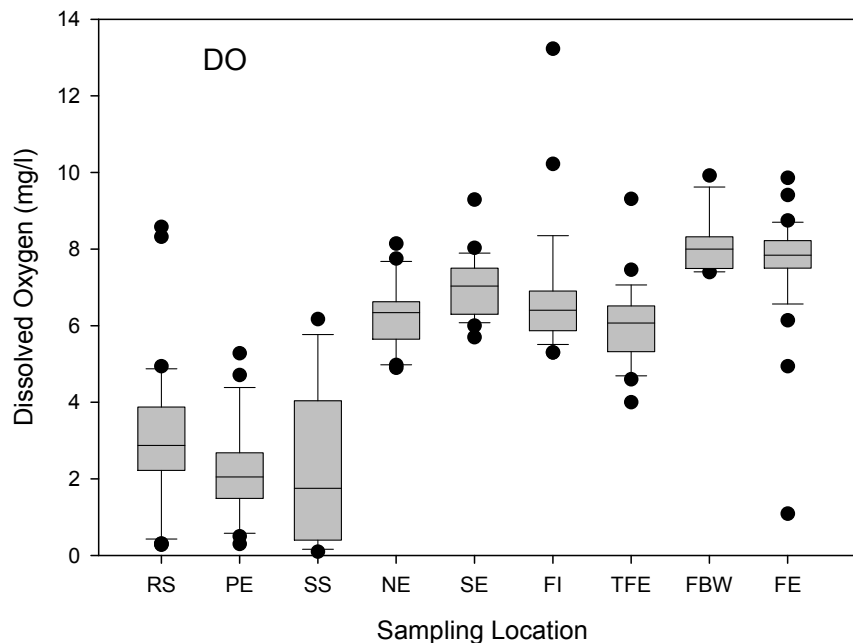


Figure 4-8 Dissolved oxygen concentrations at different Plant locations.

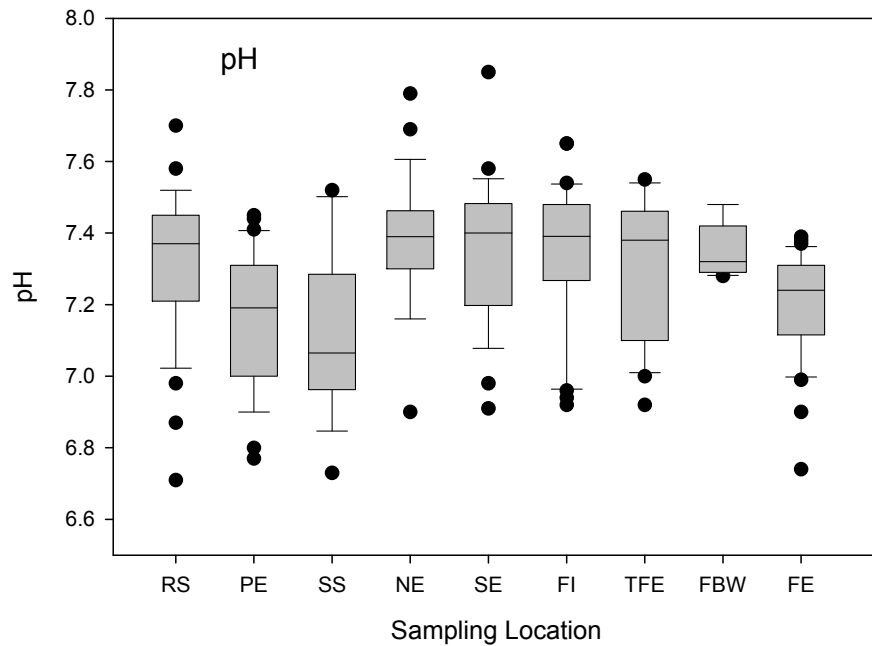


Figure 4-9 pH levels at different Plant locations.

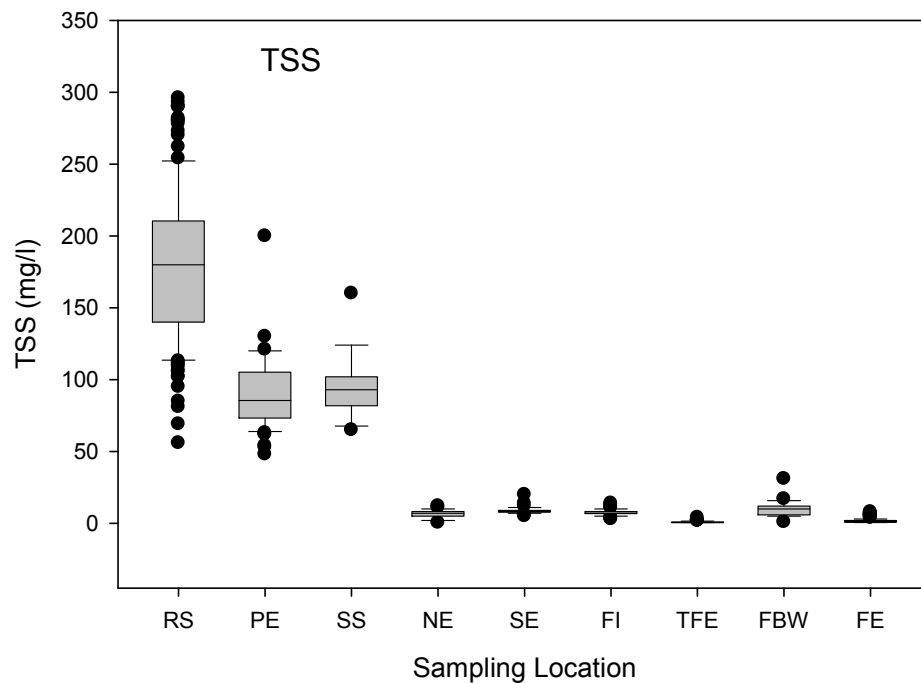


Figure 4-10 Total suspended solids (TSS) at different Plant locations.

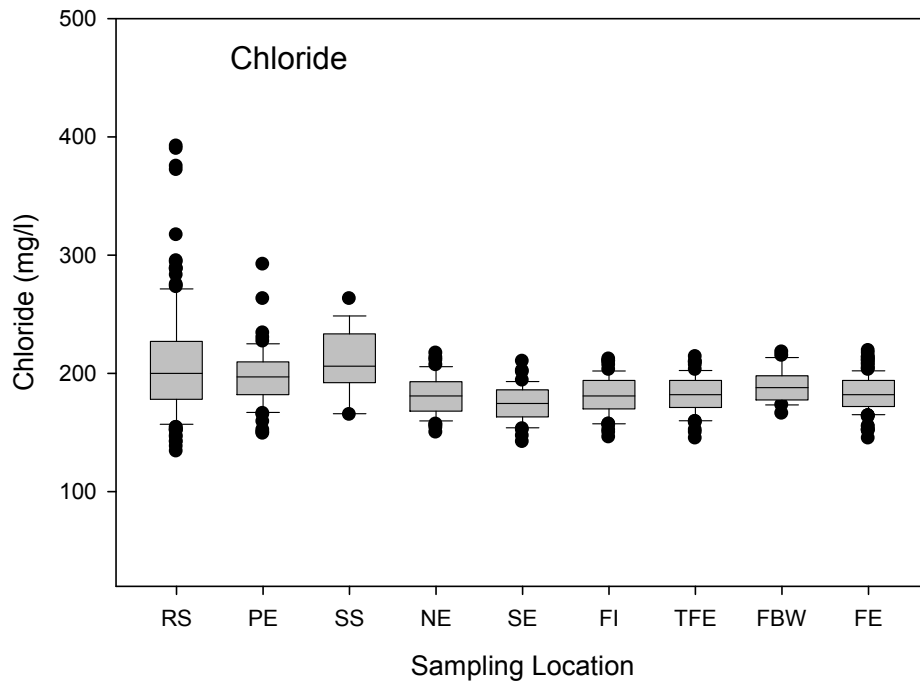


Figure 4-11 Chloride at different Plant locations.

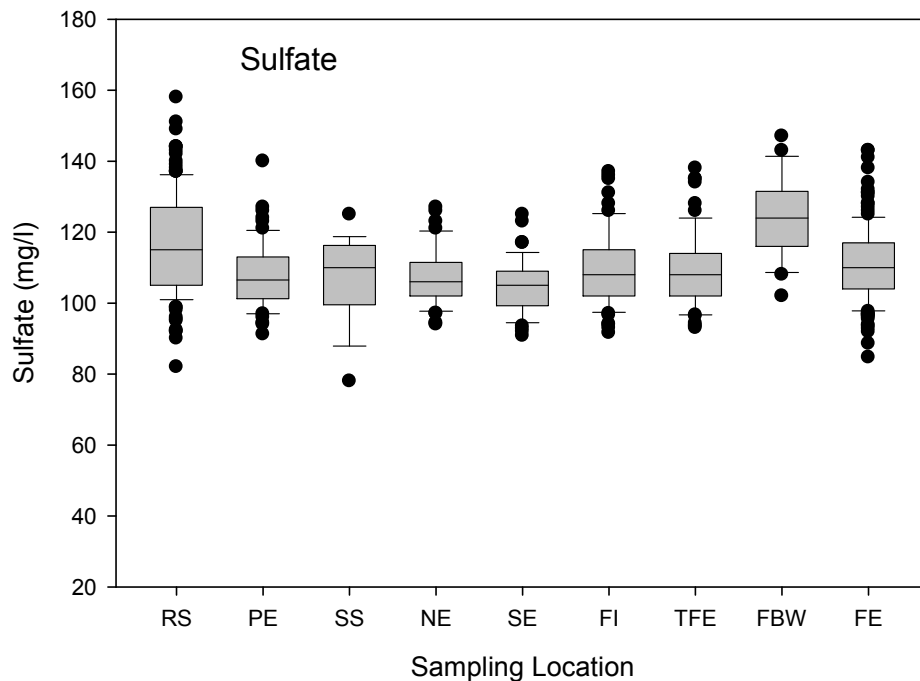


Figure 4-12 Sulfate at different Plant locations.

4.4 24-HOUR SAMPLING RESULTS

Twenty-four hour mercury sampling was conducted on three separate dates. Samples were collected at a 4-hour frequency to understand the intra-day variability of mercury within the Plant (Figure 4-13). This 24-hour data set is important for evaluating the mercury mass

balance information because grab samples collected during the main part of the study were always collected at approximately the same time each day (between 7 and 10am). Data collected from the intensive sampling events show a distinct afternoon-early evening peak in raw sewage concentrations especially for total mercury and dissolved mercury. Afternoon concentrations may be nearly twice as high as morning concentrations. These temporal trends also match TSS concentrations, which peak at the same time as total mercury concentrations. Methylmercury concentrations are relatively uniform over the course of a day. Because of water and sludge residence times within the Plant (from hours to weeks) and internal cycling, the change in influent concentrations has practically no impact on the intra-day values of the effluent concentrations of both total and methylmercury (Figure 4-14).

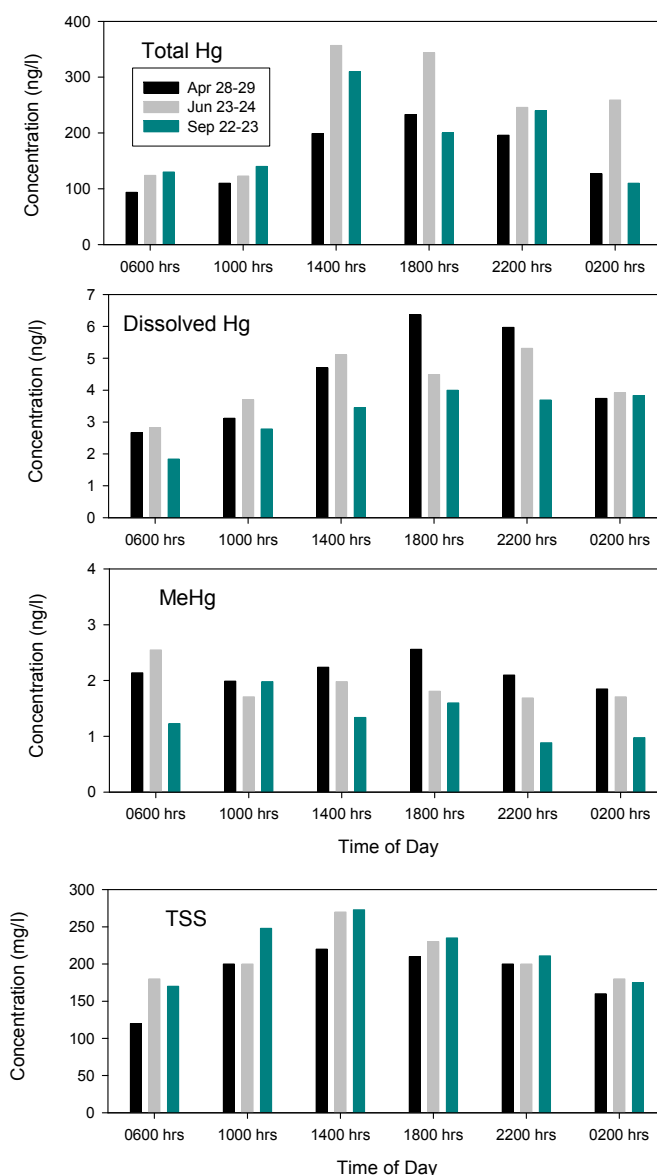


Figure 4-13 Mercury species and TSS concentrations at different sampling times during the day. These grab samples were collected on three dates during the study.

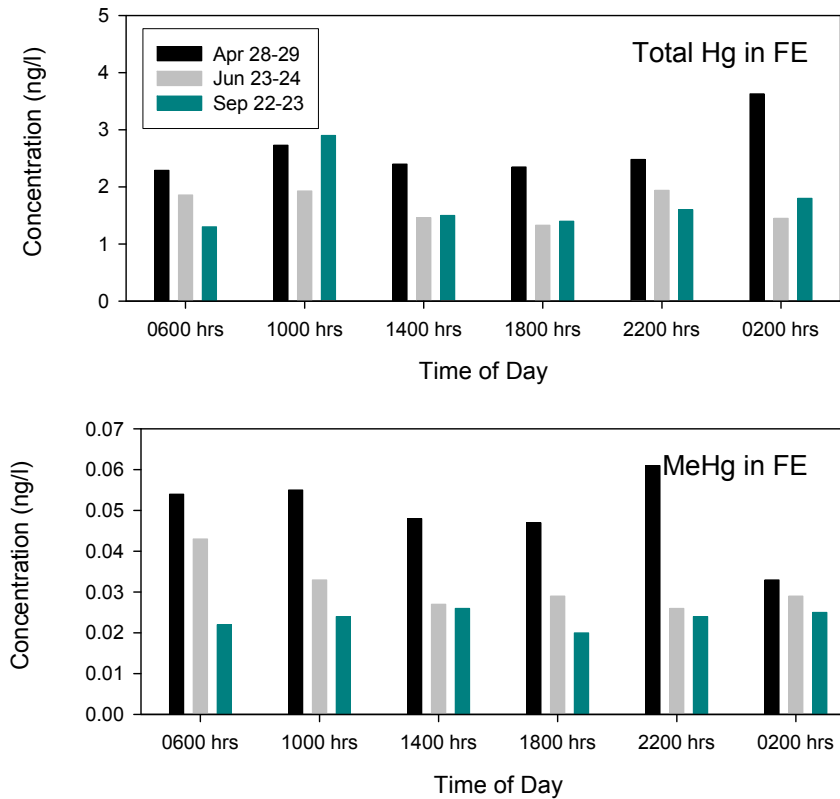


Figure 4-14 Total and methylmercury concentrations in the final effluent at different sampling times.

4.5 COMPARISON OF COMPOSITE AND GRAB SAMPLES

As part of a parallel study performed in the Plant, composite mercury samples were collected for RS over a period of time that overlaps with the detailed mercury fate and transport study described in this report. As noted earlier, composite samplers were not used for this study because the composite sample collection did not adhere strictly to the ultraclean sampling protocols (EPA method 1669). However, composite sample data on Hg at RS still provide meaningful information because these concentrations are usually fairly high (i.e., almost always over 100 ng/l). A comparison of grab sample data and composite sample data are shown in Figure 4-15. On average, composite sample data are about 1.7 times higher than grab sample data. The 24-hour trend in mercury concentrations can explain these data because grab samples were consistently collected around 8 am, whereas the highest concentrations of mercury were observed later in the day.

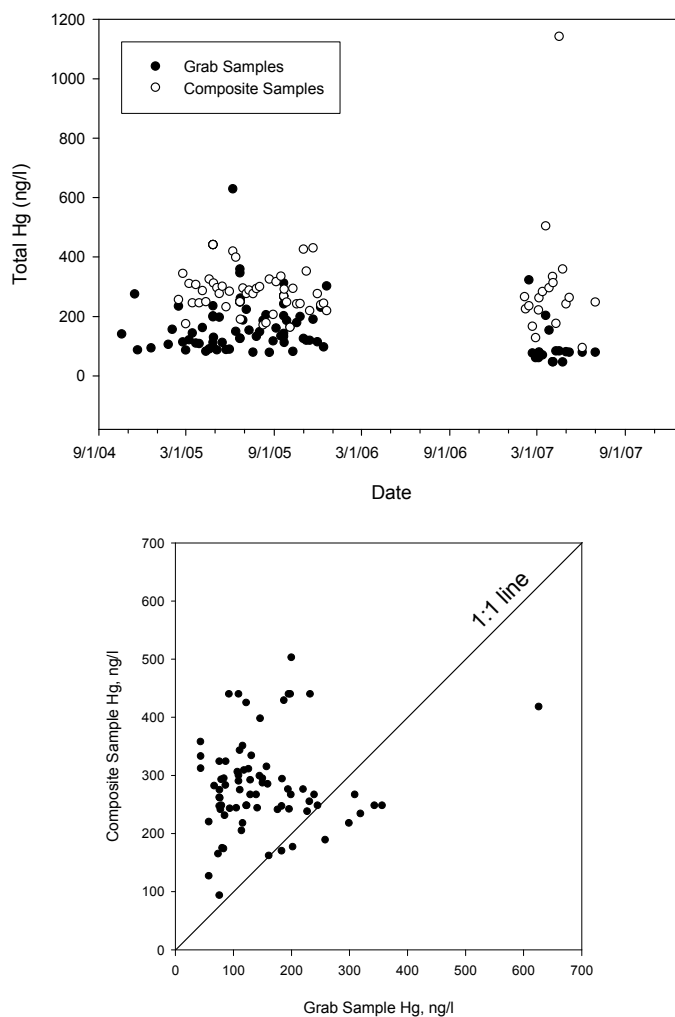


Figure 4-15 Comparison of total mercury concentrations from grab samples and from 24-hour composite samplers.

4.6 MASS BALANCE CALCULATIONS

An estimate of the mercury mass balance was performed for each day that sampling was conducted. These calculations show that total mercury in digested sludge (DS) potentially accounts for most of the mercury removed from raw sewage (Figure 4-16). Note that there are discrepancies between the mass inflows in raw sewage and in digested sludge: total mercury export in sludge is calculated to be higher than the inflow in RS, based on grab sample concentrations. This may be due to uncertainties in mercury concentration and flow measurements especially in the sludge stream, as well as to inter- and intra-day variability in mercury concentrations, some of which are shown in Figures 4-13. The effect of intra-day variation for total mercury can be partially captured by assuming that composite concentrations are a better representation of influent loads than the grab samples as shown using the dashed line in Figure 4-16. In this case, the influent total mercury loads have been revised upward on average by a factor of 1.7, and the influent loads and sludge exports are in

closer agreement. Total mercury recovered in sludge is slightly lower than the total mercury inflow calculated based on the composite data.

Based on weekly concentration data and daily average flow data, influent loads of mercury in raw sewage average 63.6 g/day (or 23.2 kg/yr), uncorrected for intra-day variation in concentration. The final effluent loads based on concentrations and measured outflow volumes average 0.97 g/day (or 0.35 kg/year). The mass balance and the associated uncertainty are discussed in greater detail below.

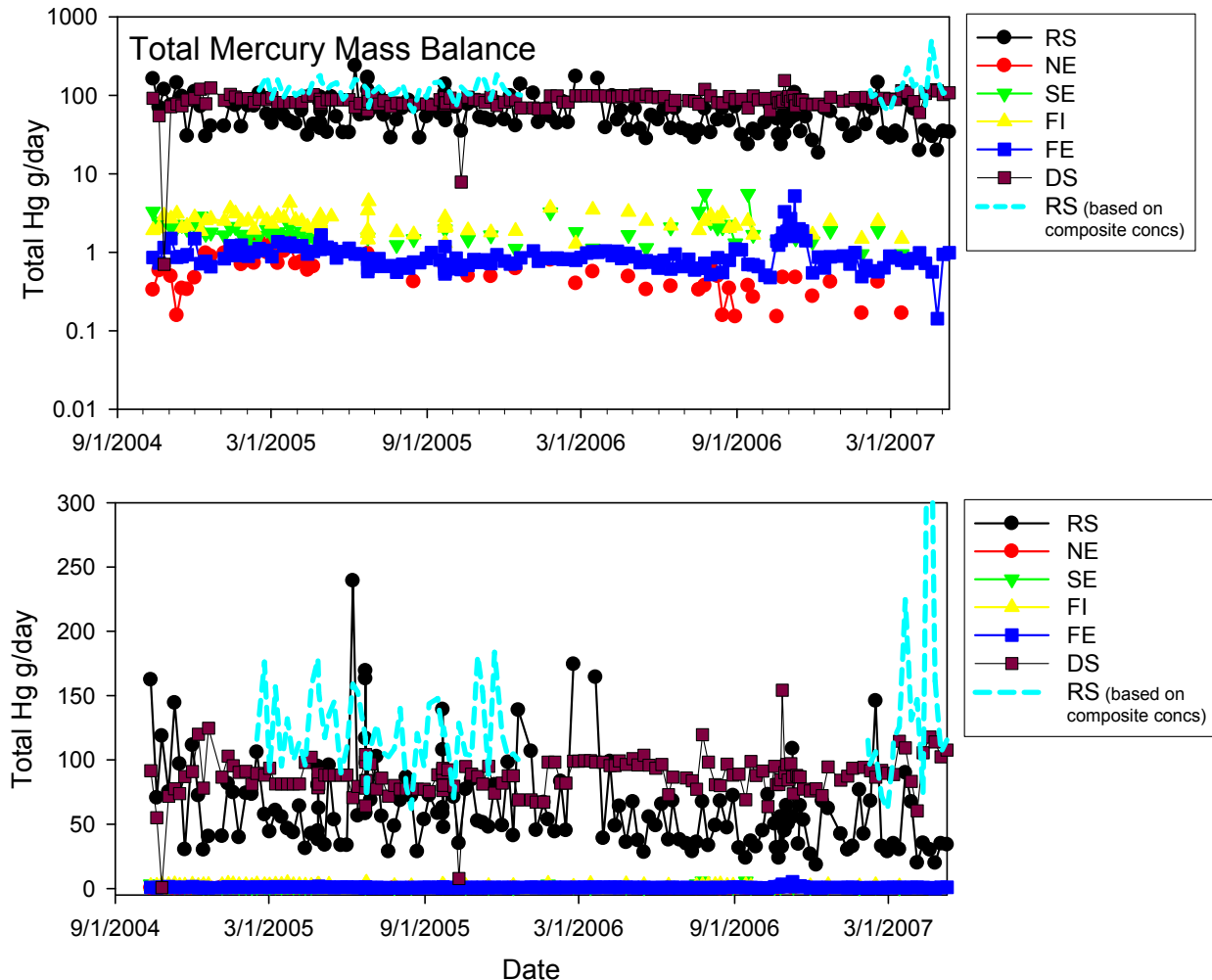


Figure 4-16 Mass balance for total mercury in the Plant (Note the different Y-axis scales; log scale on the upper graph and normal scale on the lower graph).

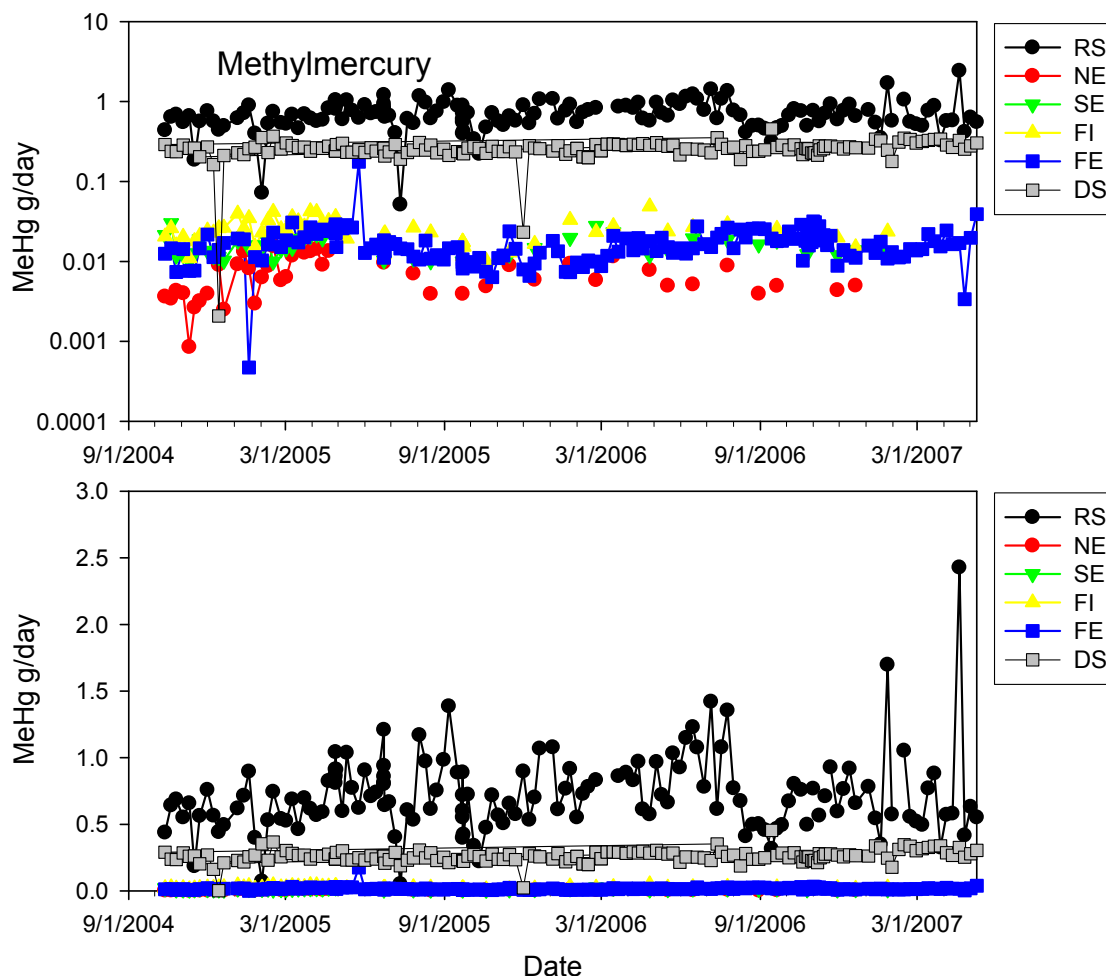


Figure 4-17 Mass balance for methylmercury in the Plant.

For methylmercury, composite data were not available to perform a similar comparison in Figure 4-17. Based on 24-hour sampling results (Figure 4-13 and Figure 4-14), methylmercury does not vary significantly throughout the day. Therefore, grab samples for methylmercury should be representative of the daily concentrations. Daily mass balance calculation indicated not all methylmercury in inflow was recovered in digested sludge (Figure 4-17). Based on the daily mass balance, methylmercury inflow averages 0.72 g/day. However, only 36% of this inflow amount (0.26 g/day) was recovered in the digested sludge. Methylmercury in plant outflow averages 0.02 g/day. The discrepancy in mass balance (0.44 g/day or 61%) could be attributed to multiple factors including the lack of accurate methylmercury concentrations in the sludge (only a total of 20 samples are available for the study period) as well as loss or demethylation of methylmercury during treatment processes.

4.7 MERCURY LOAD VARIATION AND ESTIMATION OF UNACCOUNTED MASS

A simplified long-term mass balance within the Plant was developed based on the average flow and concentrations at the available locations to better quantify the loss of mercury and uncertainties in mercury loadings in various treatment processes. There are two common formats in which variation in measured parameters can be expressed. Consider the mean

value of the mercury concentration $Conc_{mean}$ and the mercury load $Load_{mean}$. These will be symbolically written as $Mean$. Its variation can be expressed using either confidence interval format $Mean \pm 95\% CI$ or the standard deviation format $Mean \pm SD$. Both the confidence and standard deviation formats are widely used. The question is not deciding which format is more or less correct but rather deciding what the data are to be used for. The format $Mean \pm 95\% CI$ describes the upper and lower 95% confidence interval about the mean. The formula used to evaluate it is described in the Appendix. The $\pm 95\% CI$ term represents the uncertainty of how precisely the mean of the measured load represents the true value of the population mean. The format $Mean \pm SD$ is the proper format needed for data that is to be summed or multiplied together in a mass balance calculation.

The flow data in Table 4-3 are the average of daily flow measurements for the study period. Total and methylmercury concentrations shown in Table 4-3 are the mean and 95% confidence interval (CI) for all available measurements in the study period. Load estimates at the sampling locations are shown in Table 4-4, and schematically in Figure 4-18.

Table 4-3
Average water and sludge flow volumes at various locations

	Flow (mgd)		THg Concentrations (mean $\pm 95\% CI$)	MeHg concentrations (mean $\pm 95\% CI$)
Flow to primary	120.3	RS (ng/l)	144.8 \pm 13.5 ^a 261.5 \pm 10.7 ^b	1.63 \pm 0.10
Flow to nitrification	38.2	PE (ng/l)	87.6 \pm 9.9	1.51 \pm 0.18
Flow to secondary	90.9	SS (ng/l)	74.4 \pm 15.7	1.16 \pm 0.27
Flow to infiltration	121.0	FI (ng/l)	5.0 \pm 0.3	0.051 \pm 0.004
Total outflow	117.9	FE (ng/l)	2.19 \pm 0.19	0.037 \pm 0.002
Sludge flow from primary	0.383	PS (ppb)	56.2 \pm 38.7	0.119 \pm 0.074
Sludge flow from thickening	0.447	TAS (ppb)	37.5 \pm 14.5	0.131 \pm 0.069
Sludge flow from anaerobic digester	0.867	DS (ppb)	26.1 \pm 3.6	0.077 \pm 0.020

a. grab sample concentrations b. composite sample concentrations

Table 4-4
Long-term average mass balance at various Plant locations assuming average flow volumes at measured flow locations

	Total Hg loads (g/day) (mean ± 95% CI)	MeHg loads (g/day) (mean ± 95% CI)
Plant influent	111.9 ± 10.4 ^a or 118.9 ± 4.9 ^b	0.74 ± 0.15
Flow to "Secondary"	30.1 ± 3.4	0.52 ± 0.06
Flow to "Nitrification"	10.7 ± 2.3	0.17 ± 0.04
Primary settling sludge	81.4 ± 56.0	0.17 ± 0.11
Thickened sludge	63.4 ± 24.5	0.22 ± 0.12
Digested sludge	85.2 ± 11.8	0.25 ± 0.07
Flow to filter	2.3 ± 0.14	0.02 ± 0
Total plant effluent	0.97 ± 0.08	0.02 ± 0

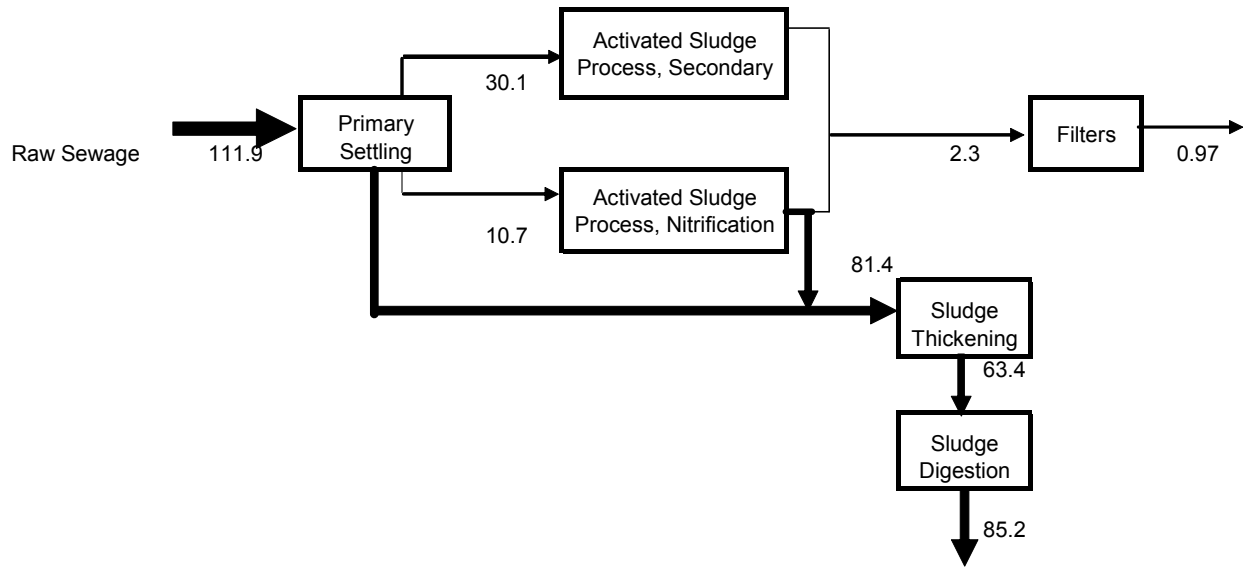
a. based on grab sample concentrations adjusted by 1.7

b. based on composite sample concentrations

The long-term mass balance calculation indicates most total mercury is recovered in the digested sludge (76 % recovery; Table 4-4). The unaccounted portion of total mercury is due to large uncertainties in the loading estimates of primary sludge and thickened sludge. The apparent unaccounted mass is discussed in the next section. Generally, it seems primary settling does not result in significant mercury mass imbalance. For methylmercury, a larger imbalance was observed through the treatment processes. The largest loss seems to occur in the BNR and sludge thickening processes (0.47 g/day). Overall methylmercury in inflow recovered in the digested sludge is low (34%) with an unaccounted mass of 0.49 g/day. The observed large loss in "Secondary" and "Nitrification" is supported by the quad sampling data, which indicated generally decreasing methylmercury concentrations from quad 1 to quad 4 for both SE and NE.

Intra-day flow data associated with the influent was available for limited periods and is shown in Figure 4-19 (flow to primary tanks). These data were used to estimate the standard deviation associated with influent flow measurements, and the resulting variation in loads is shown in Tables 4-5 and 4-6. A flow rate variability of ± 27.3 mgd (based on one standard deviation) was computed. The mathematical algorithm used to multiply together two variables with standard deviations, such as the influent concentration times the influent flow rate, is described in the Appendix.

Total Mercury (g/day)



Methyl Mercury (g/day)

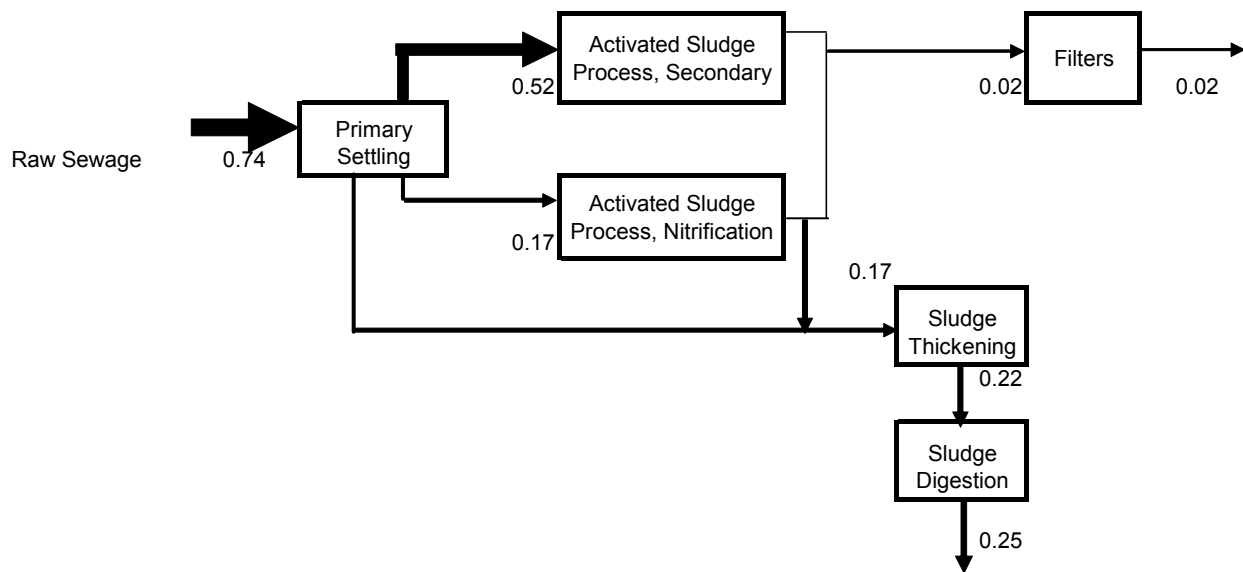


Figure 4-18 Schematic of daily average loads for total mercury and methylmercury in the Plant.

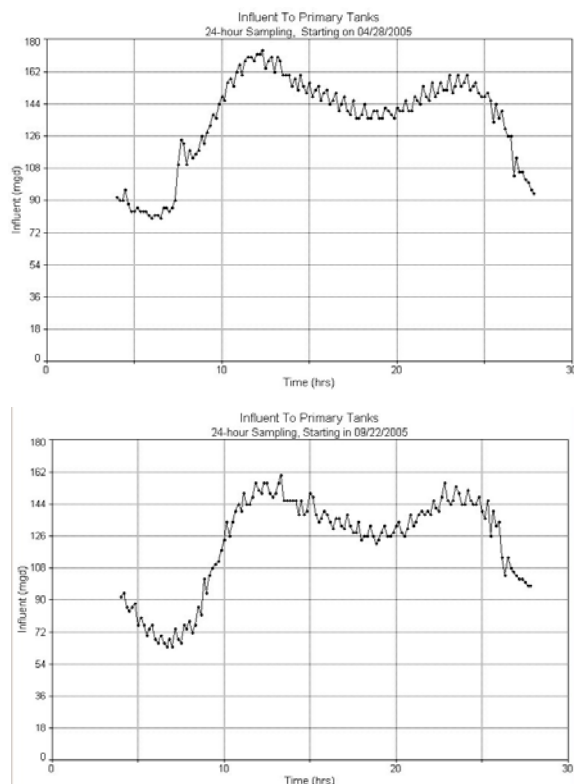


Figure 4-19 Twenty-four hour sampling of influent to primary tanks on 4/28/05 (upper plot) and 09/22/2005 (lower plot).

Table 4-5

Total mercury load estimated for raw sewage (RS), digester sludge (DS), and final effluent (FE).

The $\pm SD$ symbol indicates the interval that would encompass 68% of the mercury load measurements.

Total Hg	Conc (<i>Mean \pm SD</i>)	Flow (mgd)	Load (<i>Mean \pm SD</i>) (g/day)
Raw sewage	144.84 \pm 82.82 ^a (ng/l)	120.3 \pm 27.3 ^c	112. \pm 70.5 ^{bc}
Final effluent	2.19 \pm 1.19 (ng/l)	117.9	0.97 \pm 0.53
Digested sludge	26.1 \pm 7.8 (ppb)	0.867	85.2 \pm 25.6

a. based on grab sample concentrations

b. based on grab sample concentrations, adjusted by 1.7

c. standard deviation is based on total flow measurements to primary tanks (PT413Z) recorded every 10 minutes for 24 hours on 09/22/2005 (see Figure 4-b)

Table 4-6

Methyl-mercury load estimated for raw sewage (RS), digester sludge (DS), and final effluent (FE). The $\pm SD$ symbol indicates the interval that would encompass 68% of the methyl-mercury load measurements.

MeHg	Conc (<i>Mean $\pm SD$</i>)	Flow (mgd)	Load (<i>Mean $\pm SD$</i>) (g/day)
Raw sewage	1.63 ± 0.63^a (ng/l)	120.3 ± 27.3^c	0.74 ± 0.34^{bc}
Final effluent	0.037 ± 0.014 (ng/l)	117.9	0.016 ± 0.006
Digested sludge	0.077 ± 0.042 (ppb)	0.867	0.25 ± 0.14

a. based on grab sample concentrations

b. based on grab sample concentrations, adjusted by 1.7

c. standard deviation is based on total flow measurements to primary tanks (PT413Z) recorded every 10 minutes for 24 hours on 09/22/2005 (see Figure 4-b)

Average daily mercury loads of final effluent and raw sewage were compared. Results of the mass balance calculations for total mercury and methylmercury are listed in Table 4-7. A brief description of the algorithm for this calculation is given in the Appendix. For example, the sum of the mean mercury loads from the final effluent and digested sludge were added together and then subtracted from the mean value entering in raw sewage. This results in a 25.8 ± 75 g/day difference in the total mercury that is unaccounted for by these simple mass balance calculations. However, the resultant one-standard deviation calculation of the unaccounted mercury load indicates that the actual unaccounted for difference could be a deficit of 49.2 g/day of total mercury or a surplus of 101g/day of total mercury. The greatest contribution to this uncertainty is from the variation of mercury in the raw sewage influent. An examination of the intra-day variability of mercury within the Plant described in Section 4.4 demonstrates that mercury concentrations can vary by a factor of three over a 24 hour period and even greater variations occur over the year.

The high variability in influent concentrations of mercury can also be seen by examining the coefficients of variation (cv) in Table 4-2. The cv for raw sewage is 0.57. In contrast, the digester sludge and final effluent concentrations have a relatively low coefficient of variation. This low variability is due to the long residence time and homogenization within the treatment process. It is a problematic exercise to accurately perform a mass balance on mercury output values having a substantially long, monthly time scale when comparing this to the relatively short, hourly time scale variation in the mercury input from raw sewage.

Table 4-7

Total mercury and methyl-mercury loads unaccounted when estimating a mass balance between raw sewage input and final effluent and digested sludge outputs. The $\pm SD$ symbol indicates the interval that would encompass 68% of the mercury and methyl-mercury load estimates.

Component	Total Hg Load (<i>Mean $\pm SD$</i>) (g/day)	MeHg Load (<i>Mean $\pm SD$</i>) (g/day)
Unaccounted for	25.8 ± 75^c	0.47 ± 0.37^c

4.8 CORRELATIONS OF MERCURY WITH OTHER PARAMETERS

The only correlation found between mercury species and ancillary parameters was with TSS. The observed variation in total mercury in the RS can be partially explained by variations in TSS (correlation coefficient of 0.47; $p < 0.05$). Mercury concentrations at various locations in the treatment plant generally corresponded with TSS concentrations (e.g., in Figure 4-1 and Figure 4-5). In particular, the increase in total mercury concentrations in the filter backwash is indicative of the fraction trapped on particulates. Daily estimates of mercury loads at most locations sampled in the treatment plant have a moderate to high correlation with estimates of TSS loads. Data and correlations for key locations in the plant are shown in Figure 4-20.

Average plant inflow and outflow volumes were similar between dry (May through September) and wet (October through April) months, although wet months did have a higher incidence of high inflow spikes. No correlations were observed between inflow and outflow volumes and mercury concentrations (Figures 4-21 and 4-22). Final effluent data show a period of elevated total mercury concentrations due to a filter bypass event, indicating the important role of filtration in the final removal of mercury from the treatment plant (Figure 4-22, lower graph). Influent methylmercury concentrations were not correlated with plant inflow volume (Figure 4-23). Methylmercury concentrations seem to be higher in warmer months.

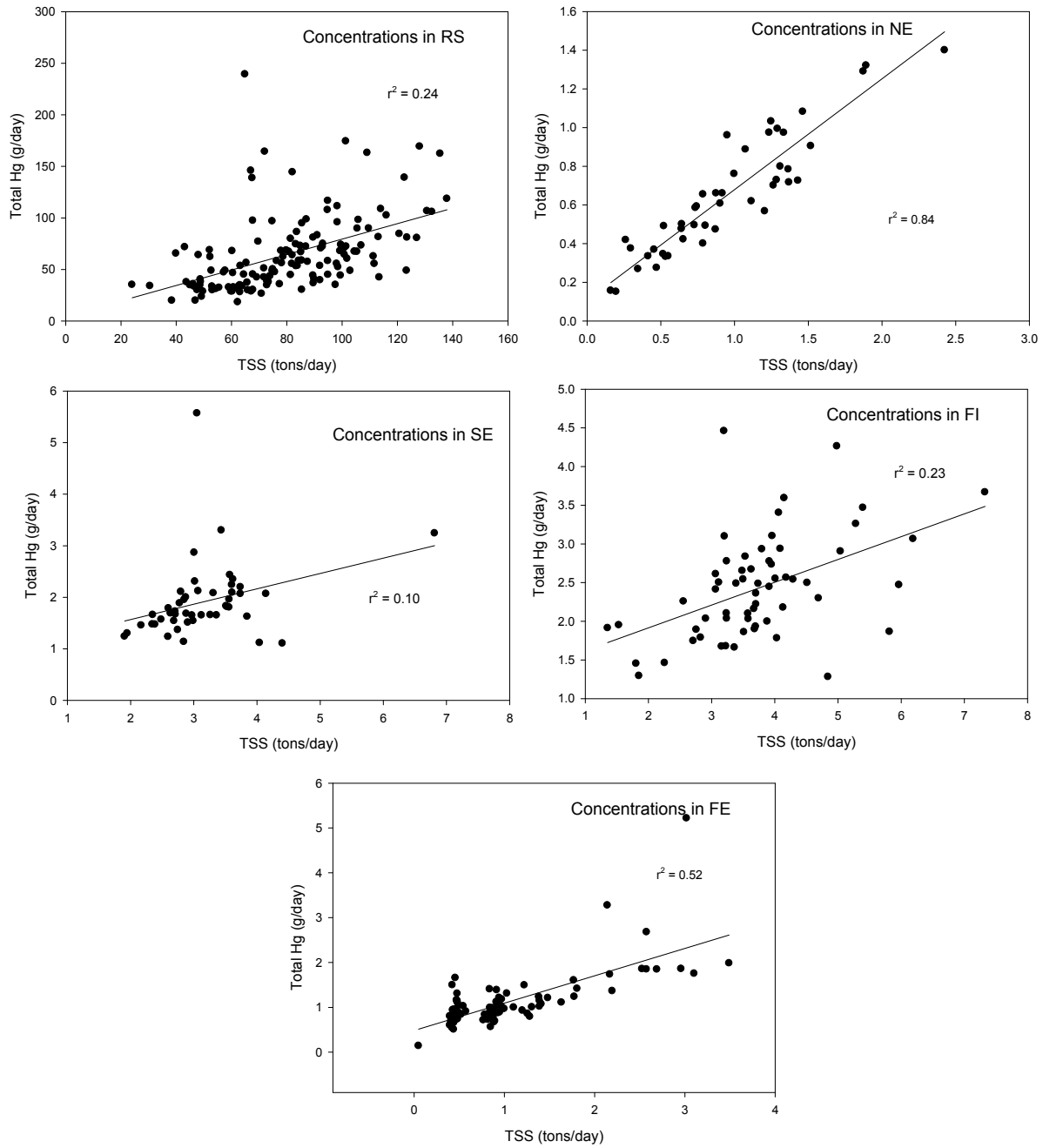


Figure 4-20 Total mercury and TSS concentrations at key Plant locations.

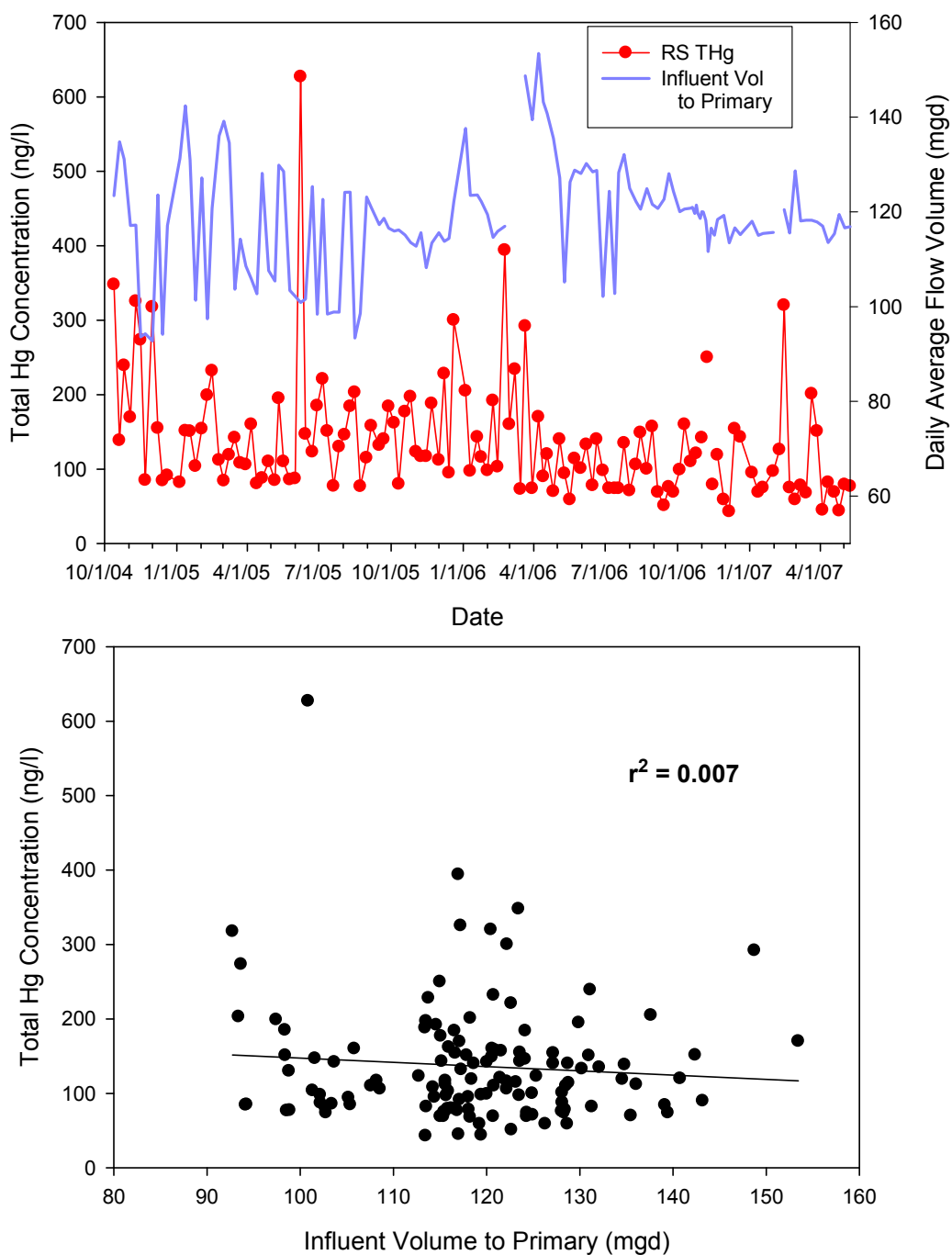


Figure 4-21 Flow and total mercury in Plant influent.

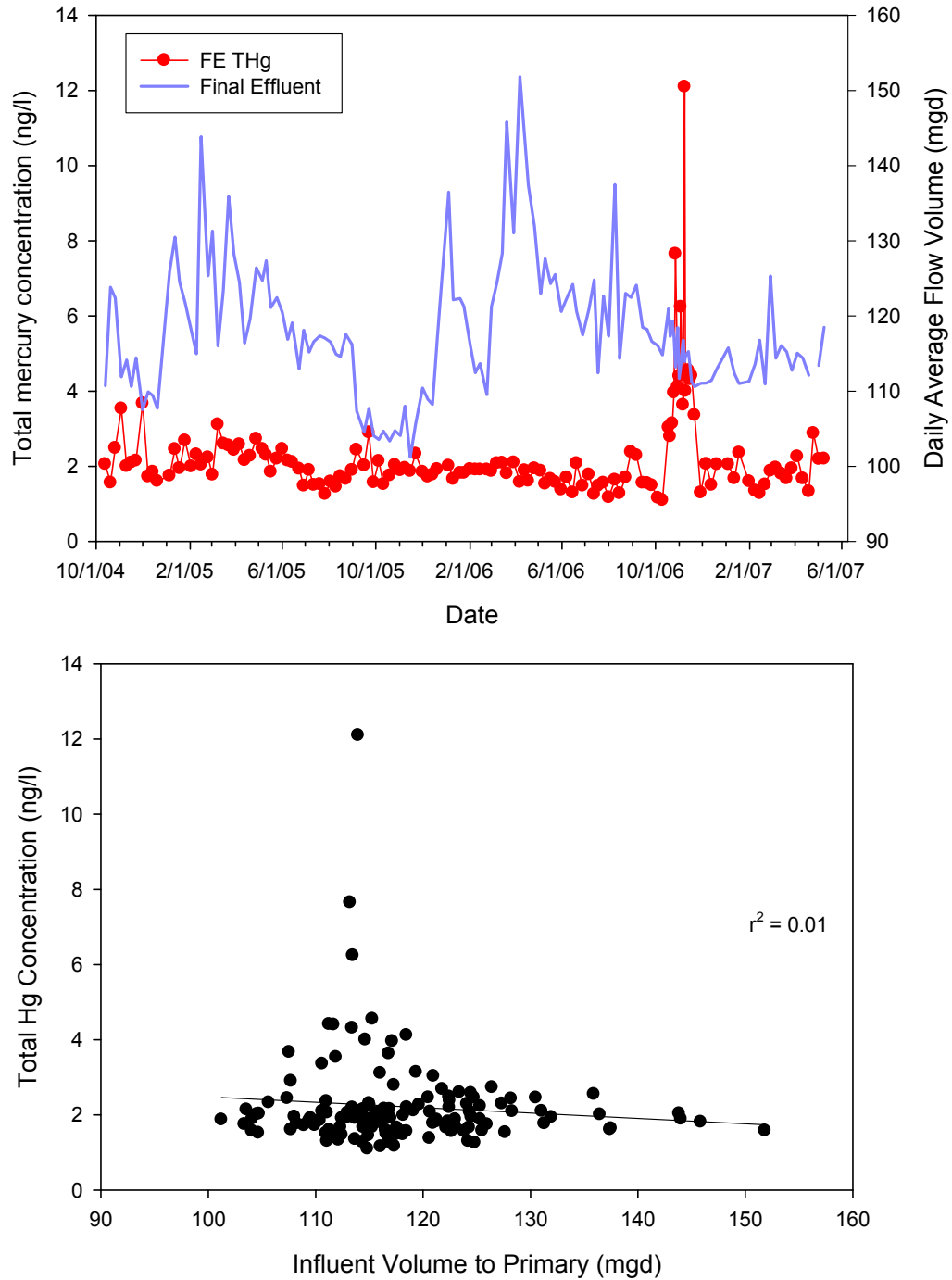


Figure 4-22 Flow and total mercury in Plant effluent.

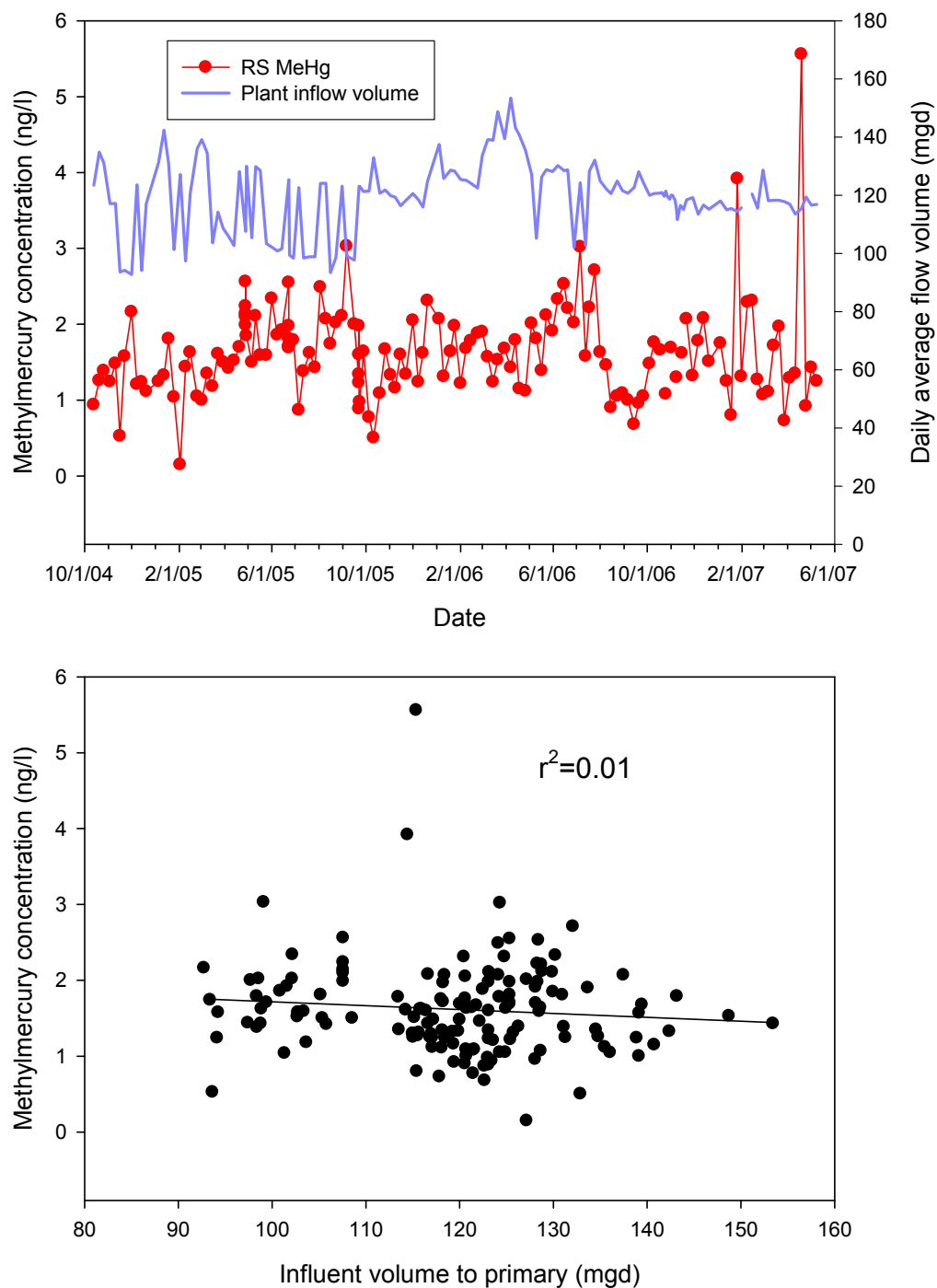


Figure 4-23 Flow and methylmercury at the Plant influent.

4.9 TREND ANALYSIS OF MERCURY CONCENTRATION

A trend analysis using the Mann-Kendall algorithm was performed with the total mercury and methylmercury concentrations in the raw sewage (RS) and final effluent (FE) data as a function of time. The lower and upper 95% confidence limits of the mercury versus time

slope are first calculated using Sen's slope indicator and the significance of the slope is tested using the Mann-Kendall algorithm (discussed in the Appendix). The raw sewage and final effluent concentrations of total mercury were statistically found to have downward trends in concentration over time. A statistical summary of Sen's confidence limits and Mann-Kendall trend tests for the total mercury data are listed in Table 4.8. A visual examination of the total mercury concentrations versus time in Figures 4-21 and 4-22 also suggests a decrease in concentration with time.

A Mann-Kendall statistical test was also performed using the methylmercury (Me-Hg) concentrations versus time in the raw sewage and final effluents. However, no trend was found with the raw sewage Me-Hg concentration data and a small upward trend was found with the Me-Hg concentration data for the final effluent. A summary of Sen's confidence limits and Mann-Kendall trend tests for the Me-Hg data are listed in Table 4.8.

The above analysis was repeated using a seasonal trend analysis routine, which is described in the Appendix. All mercury and methylmercury concentration data were assigned a season indicator by quarter (i.e., Q1 for Jan-Mar dates; Q2 for Apr-Jun dates, etc.) and then analyzed using the seasonal Kendall test. There was only a slight change in slope estimates and no change from the previous tests occurred in the test-of-significance for trend. Table 4.8 lists all of the seasonal Kendall test results for both total Hg and Me-Hg. A further seasonal test was performed by assigning each sample value a month-of-the-year season indicator (i.e., M1 for Jan, M2 for Feb, etc.). The seasonal Kendall tests were repeated with identical results to that of the quarterly test. The monthly seasonal analysis has not been included.

Table 4-8
Mann-Kendall trend analysis and seasonal trend analysis of mercury concentration versus time.

	RS Total Hg	RS Me-Hg	FE Total Hg	FE Me-Hg
Number of values	132	131	126	140
Sen's lower 95% confidence limit of slope	-0.1057 ng/l/day	-0.00014 ng/l/day	-0.00087 ng/l/day	0.0000033 ng/l/day
Sen's upper 95% confidence limit of slope	-0.0458 ng/l/day	0.00040 ng/l/day	-0.00041 ng/l/day	0.000017 ng/l/day
Median value of slope	-0.076 ng/l/day	0.00012 ng/l/day	-0.00064 ng/l/day	0.00001 ng/l/day
Test of Mann-Kendall trend analysis	Accept alternate H_{a2} of downward trend	Accept null H_o of no trend	Accept alternate H_{a2} of downward trend	Accept alternate H_{a1} of upward trend
Median value of slope with seasonal effects removed	-0.074 ng/l/day	0.00013 ng/l/day	-0.00066 ng/l/day	0.000011 ng/l/day
Test of Mann-Kendall seasonal trend analysis	Accept alternate H_{a2} of downward trend	Accept null H_o of no trend	Accept alternate H_{a2} of downward trend	Accept alternate H_{a1} of upward trend

The Mann-Kendal test considers four hypotheses: null H_o : no trend is present; alternative H_{a1} : and there is an upward trend present; alternative H_{a2} : there is a downward trend present. These data were then used with the Mann-Kendall seasonal trend analysis. Each data value was assigned to one of the four quarterly time periods (i.e., Q1, Q2, Q3, Q4). All tests are performed at the 95% confidence level.

4.10 FINDINGS RELATED TO THE KEY STUDY QUESTIONS

The following is a discussion of the findings in the context of the major research questions identified in Chapter 2.

1. Can the variability in influent mercury in the plant be correlated with other factors (such as flow, season, etc.)?

Mercury concentrations are variable over the course of a single day but show little change over the entire sampling period. No correlation with concentration and flow was observed. Mercury concentrations were found to be correlated with TSS concentrations in the influent ($r = 0.47$; $p < 0.05$).

2. What is the sample measurement variability, especially of particle-associated mercury species? Is the inflow concentration variability swamped by sample measurement variability?

Data across the treatment plant, especially where lower concentrations are observed, show remarkably consistent results over the study period. This suggests low sample measurement variability. Influent concentrations are naturally variable, with part of the variability related to particle-associated mercury and part of the variability caused by sampling only at one time of the day.

3. Do the unique conditions that occur in wastewater treatment, notably anoxic conditions during activated sludge treatment, affect the methylation of mercury?

The data did not show evidence of net mercury methylation in the treatment plant. Sulfate concentrations and anaerobic conditions are sufficient to promote methylation. However BNR quad samples showed a trend of decreasing methylmercury, indicating no effect on net methylmercury production in the activated sludge treatment. Digested sludge samples indicated occasional increases in methylmercury concentration relative to the primary and thickened sludge, although the data to evaluate the change were limited.

4. Are mercury concentrations related to other measurable water chemistry parameters in the treatment process (e.g., suspended particles, sulfide concentrations, etc.)?

Mercury concentrations were correlated with TSS at several locations, but not with any other chemical parameter that was measured.

5. Is the total mercury removal from the raw sewage concentrated in the sludge or is some of it lost to volatilization?

The sludge appears to be the sink for most of the influent total mercury in the Plant. Volatilization is not expected to be significant, in part because concentrations of dissolved mercury (which include dissolved gaseous mercury) are a very small fraction of the total mercury in most process steps. However the discrepancy of mercury in the influent and digested sludge suggested some of the total mercury may be lost through volatilization, although uncertainties could contribute a large percentage of this discrepancy.

6. Which process steps are most effective at removing the different forms of mercury from the wastewater, and through what mechanism?

Settling of particulates appears to be the most effective mercury removal mechanism. The greatest reductions in mercury concentrations occur following the secondary and nitrification process steps.

7. How variable is the mercury removal by individual treatment process steps for daily and seasonal changes in flow?

Mercury removal appears to be fairly stable and there were no systematic changes in efficiency with season. Effluent concentrations were also relatively uniform, even though influent concentrations vary considerably over the course of the day.

8. Where parallel treatment paths exist, do they behave similarly with respect to mercury removal?

Parallel treatment paths (i.e., the “Secondary” and “Nitrification” paths within the BNR process) are almost identical to each other in terms of mercury removal.

9. How accurately can mass balances be determined for the plant as a whole, and for individual processes, given the inherent variability and measurement error in flow and concentrations?

Because the decrease in concentration across the entire plant is very large (~99%), the mass balances for the influent and effluent can be determined fairly robustly (<10% uncertainty, Table 4-4). Mass balances over individual process steps particularly in sludges are known with less precision, except processes such as secondary settling, which

result in large percent declines in total mercury. Therefore overall mass balances for processes are subject to relatively large uncertainty.

4.11 SUMMARY

- Overall, the Plant is highly efficient at removing total mercury from raw sewage, with nearly 99% removal of inflow concentrations. Reduction in mercury species is in the following order: Total Hg (99%) > MeHg (97%) > Dissolved Hg (50%); most of the effluent mercury is in dissolved form.
- Based on weekly concentration data and daily average flow data, and correcting for intra-day variation influent loads of total mercury in raw sewage average 112 g/day. The final effluent loads based on concentrations and measured outflow volumes average 0.97 g/day (or 0.35 kg/year), a reduction of nearly 99%.
- Total influent mercury and removal of mercury at various process stages is correlated with TSS. Correlations were not found for any other chemical parameter measured. Grab-sample mercury concentrations were also not correlated with daily average flows.
- There was no evidence of mercury methylation in the Plant treatment process, i.e., the Plant does not add to the toxicity or bioavailability of the mercury flowing through it. Although there is a great deal of evidence of mercury methylation under sulfate reducing conditions in natural waters, there appears to be no net methylmercury added to wastewater during treatment.
- Concentrations of methylmercury within the Biological Nutrient Removal process, although variable across dates, did not show a consistent pattern that could be explained by the alternating aerobic and anoxic conditions within the process.
- Sludge concentrations of total mercury on a dry-weight basis were much higher than aqueous concentrations because of the presence of mercury in the suspended particulate phase.
- The 24-hour intensive sampling indicates elevated total mercury concentrations between 2 pm and 10 pm. This may indicate certain source types (e.g. commercial/industrial vs. residential) and also suggests the importance of adhering to a specific sampling schedule especially for measurements in raw sewage. Twenty four-hour composite sample data are supportive of these grab sample results; raw sewage composite mercury concentrations are always higher than morning grab sample values.
- There is potential for mass balance errors because the grab sampling does not capture the intra-day range in concentrations, and relatively large uncertainties exist in the sludge flows and concentrations. Even so, it does appear that flows in digested sludge can account for the great majority of the total mercury removed from wastewater at the Plant.

5.0 CONCLUSIONS AND LESSONS LEARNED

The mercury fate and transport study in the San Jose/Santa Clara Water Pollution Control Plant has accomplished the major objectives stated in Chapter 3. These objectives are restated and the relevance of the study findings for each objective is discussed below.

5.1 UNDERSTAND MERCURY REMOVAL MECHANISMS IN DIFFERENT PLANT PROCESS OPERATIONS

The vast majority of mercury in the Plant influent is present in the particulate form. The removal of this mercury occurs in process steps that are associated with removal of suspended solids. Thus, there is nearly a hundred-fold reduction in total mercury as well as suspended solids concentrations following passage through the parallel Biological Nutrient Removal (BNR) process pathways. Methylmercury follows a pattern through the various processes that is very similar to that of total mercury. Dissolved mercury decreases at many of the same process steps as total and methylmercury, albeit by smaller percentages. Overall, the efficiency of total and methylmercury removal is far greater than for dissolved mercury. These data are consistent with the known environmental behavior of mercury, where its strong sorption to particle surfaces is well documented and understood.

5.2 CHARACTERIZE MERCURY CONCENTRATION AND FORM AT VARIOUS PLANT LOCATIONS UNDER A RANGE OF REPRESENTATIVE OPERATING CONDITIONS

The data summarized in the previous chapter provide a weekly picture of mercury species and behavior at all major locations within the treatment plant over a 3 year period spanning both wet and dry seasons. No similar study of mercury fate and transport within a wastewater treatment plant has previously been reported. The data showed methylmercury removal at process steps associated with total mercury removal, with no net creation of methylmercury even under process conditions with low dissolved oxygen.

Over the time period of the study there was no meaningful seasonal pattern of flow volume dependency in the mercury concentrations. Methylmercury concentrations appear to be slightly higher in warmer months. A limited number of grab samples collected over the course of a day indicated a clear diurnal pattern, with afternoon-evening concentrations

nearly twice as high as the early morning hours. This intra-day pattern is of interest in identifying potential sources of mercury, although it does not seem to have an impact on the effluent concentrations that are most important in evaluating environmental impacts.

5.3 DEVELOP A PLANT MASS-BALANCE TO IDENTIFY CRITICAL STAGES IN THE PROCESS AND SINKS FOR MERCURY

Mercury concentration and flow data at key locations were used to estimate the mass balances of mercury at different process steps. As noted above, processes associated with suspended solids removal were also closely associated with reduction in mercury loads. Sludge flow and concentrations were used to estimate mercury loads exported from the Plant as sludge. This pathway could account for all of the mercury removed as total mercury, and about one third of the methylmercury removed. The lower recovery of methylmercury in the sludge indicates possible other pathways for methylmercury removal such as degradation to CH_4 and Hg^{2+} . The mass balance had discrepancies. However, these can be resolved since the grab sample influent data underestimate the daily average mercury concentrations in the influent, and due to measurement uncertainty in the sludge mercury concentrations.

5.4 DEVELOP A TWO-PHASED APPROACH TO DATA COLLECTION, WITH A SCREENING PHASE, AND A SECOND PHASE FOR MORE DETAILED ANALYSIS OF SPECIFIC COMPONENTS

This study was initiated in October 2004 following a screening level study that had been performed for the preceding 18 months. Results of the screening level study have been reported in the Sampling and Analysis Plan for this work (City of San Jose submission to the Regional Water Quality Control Board, September, 2004). The data collection and analysis presented in this report constitutes the detailed mercury study with mercury speciation studied at all locations within the Plant over a period of 15 months. These data resolve the major uncertainties with respect to mercury behavior in the San Jose/Santa Clara Water Pollution Control Plant.

5.5 FINAL CONCLUSIONS

The data generated by this study provide a strong technical basis to explain mercury behavior at the San Jose/Santa Clara Water Pollution Control Plant, and may provide insight into mercury behavior in other wastewater treatment plants.

Long term monitoring of the influent and effluent mercury concentrations and loads and performance of the Plant, will continue as required by the NPDES discharge permit. Data at these locations will provide requisite information on changes in mercury loading at the Plant, and will identify changes in the functioning of the Plant that impact mercury removal efficiency. Statistical calculations were undertaken to estimate the minimum frequency of sampling needed to robustly characterize the mercury-removal efficiency of the Plant.

Because the reduction in concentration across the treatment plant is so large (generally greater than 98%), it was found with a Monte Carlo analysis that 15-20 samples a year would

be adequate to characterize the change in concentration between influent and effluent.² Therefore, sampling at other locations is not recommended for long term monitoring. Several of the ancillary parameters considered here are parts of routine monitoring in the Plant.

Air sampling was considered in the original Sampling and Analysis Plan, when the removal of mercury via wastewater sludge was not fully understood, and volatilization was considered a potentially significant pathway. However, the more detailed data presented here provides a strong basis for not conducting air sampling. First, the quantity of mercury exported from the Plant in digested sludge easily accounts for the influent loads of mercury to the Plant. Second, for mercury to volatilize from water, it must be present in dissolved gaseous form. Data on all forms of dissolved mercury indicate that these are a very small component of the total mercury, especially after the BNR process (1 to 2 ng/l). Even if all the dissolved mercury were in the dissolved gaseous form, it would still not form a pool large enough to cause significant volatilization. Finally, air sampling of mercury in a wastewater environment is likely to be problematic and would require the development of new and untested sampling protocols and would likely have significant uncertainty associated with them. Available data, noted above, do not justify this additional effort and expense.

Based on the preceding discussion, the mercury fate and transport study in the San Jose/Santa Clara Water Pollution Control Plant has met its goals by addressing the key questions concerning mercury behavior in Plant processes. Monitoring at a reduced number of locations, as required in the Plant's NPDES Permit, will identify seasonal patterns if they exist. This monitoring will also capture any influent reductions due to future source control efforts. The information obtained in this unique study will provide useful guidance to Bay dischargers and direction for the San Francisco Bay Mercury TMDL.

5.6 LESSONS LEARNED

5.6.1 WASTEWATER TREATMENT:

- The fate of total mercury was highly dependent on the Plant's removal of solids.
- Plant influent total mercury concentrations fluctuate predictably over the course of a typical day while effluent concentrations do not.
- Consistent timing of grab samples enabled long-term pattern identification at the cost of skewing mass balance calculations.

² A Monte Carlo algorithm based on the bootstrap method (Lepage & Billard, 1992) was devised to simulate the effect of different sampling frequencies. The bootstrap method has the advantage over other schemes in that no additional tests or assumptions are made about the underlying statistical structure of the data. In this method, a fixed number of FE/RS measured ratios were randomly drawn from the existing sample set; the mean of the sub-sample determined, and then the sub-sample values returned back to the original set. The standard deviation of the mean ratio of FE/RS from the bootstrap simulation varies minimally for sample sizes that range between 3 to 30 measurements per year. The greatest change in the standard deviation occurs for sample sizes less than 10. The standard deviation of the mean ratio decreases much more slowly for sample size between 10 and 20. This reduced rate of change in the standard deviation suggests that there is hardly any additional gain in reducing the uncertainty of the FE/RS ratio for sample sizes greater than 20 per year. (Lepage, Raoul and Lynne Billard. 1992. *Exploring the Limits of Bootstrap*. John Wiley & Sons, Inc., New York, 426 pages.)

- The two identical BNR process units, referenced as “Secondary” and “Nitrification” removed mercury and methylmercury similarly, even though flow through “Secondary” is much higher (90.9 MGD vs. 38.2 MGD).
- Differences in methods and accuracy of flow measurements, and process recirculation loops greatly complicated accurate estimation of mass balance within the Plant.
- A capable on-site analytical laboratory greatly contributed to study success by providing immediate sample handling and analysis and direct communication with chemists when unexpected results were encountered.

5.6.2 ANALYTICAL MEASUREMENT:

- Needed to design distillation unit to provide sample volumes up to 180ml instead of the 45ml in EPA1630 although 100ml was determined to be sufficient for final effluent determinations.
- Distillation did not provide total interference removal for the ethylation of methylmercury in raw sewage. Sample dilution prior to ethylation or distillation resulted in higher recoveries.
- Use of L-cysteine as a distillation agent instead of ADPC (EPA1630) led to more consistent recoveries.
- Using Tenax material instead of Carbotrap material for ethylation traps provided equivalent trapping capability while providing extended time to analyze the traps. Carbotrap material had to be analyzed within 6 hours, Tenax material held the analyte for >48 hours.
- Distillation is typically sufficient for aqueous sample cleanup, but BNR Quad samples required extraction rather than distillation prior to ethylation even though the sample matrix was essentially aqueous.

APPENDIX A- UNCERTAINTY ANALYSIS OF SUMMING AND MULTIPLYING MEASUREMENT VARIABLES

Consider the input to a sewer plant process, such as the total load of mercury in the raw sewage. It will be assigned the symbol X_1 . The raw sewage is treated by the sewer plant, resulting in two or more endpoints. These endpoint quantities are divided into an effluent product, whose mercury load is given the symbol X_2 , and a digested sludge product, whose mercury load is given the symbol X_3 . If there is to be a mass balance between input and output loads, then the sum of X_2 and X_3 should equal to that of X_1 . The expected value of X_3 can be estimated by subtracting the expected value of X_2 from the expected input value of X_1 on a weekly basis. The expected value of any variable is also called the *Mean*.

Let the measurements taken for X_1 , X_2 , & X_3 be represented as independent, random variables. The expected values of mercury concentrations for X_1 , X_2 , & X_3 are given the symbols $E[X_1]$, $E[X_2]$, and $E[X_3]$ and the concentration variances are given the symbols $Var[X_1]$, $Var[X_2]$, and $Var[X_3]$. The standard deviation SD of a variable is determined by simply taking the square root of its variance. The standard deviation of the concentrations are given the symbols $SD[X_1]$, $SD[X_2]$, & $SD[X_3]$. Hence, the expected value $E[X_3]$, the variance $Var[X_3]$, and its standard deviation $SD[X_3]$ for mercury in the solid sludge stream can be evaluated as follows:

$$E[X_3] = E[X_1 - X_2]$$

$$Var[X_3] = Var[X_1 - X_2]$$

$$SD[X_3] = \sqrt{Var[X_3]}$$

Mood et al. (1963, pages178-181) gives the following formulas for estimating the expected value and variance of random variables that are being summed. The formulas for adding or subtracting two random variables are evaluated as follows for the expected mean, the variance, and the standard deviation:

$$E[a_1X_1 + a_2X_2] = a_1E[X_1] + a_2E[X_2]$$

$$\begin{aligned} Var[a_1X_1 + a_2X_2] &= a_1^2Var[X_1] + a_2^2Var[X_2] \\ &\quad - a_1a_22Cov[X_1, X_2] \end{aligned}$$

$$SD[a_1X_1 + a_2X_2] = \sqrt{Var[a_1X_1 + a_2X_2]}$$

The a_1 & a_2 are constant coefficients that indicate whether the j^{th} variable is being added (by setting $a_j = +1$) or subtracted (by setting $a_j = -1$) from the rest of the variables.

The formulas for adding or subtracting three random variables are evaluated as follows for the expected mean, variance, and standard deviation:

$$E[a_1X_1 + a_2X_2 + a_3X_2] = a_1E[X_1] + a_2E[X_2] + a_2E[X_2]$$

$$\begin{aligned} Var[a_1X_1 + a_2X_2 + a_3X_2] &= a_1^2Var[X_1] + a_2^2Var[X_2] + a_3^2Var[X_2] \\ &\quad + 2a_1a_2Cov[X_1, X_2] + 2a_1a_3Cov[X_1, X_3] \\ &\quad + 2a_2a_3Cov[X_2, X_3] \end{aligned}$$

$$SD[a_1X_1 + a_2X_2 + a_3X_2] = \sqrt{Var[a_1X_1 + a_2X_2 + a_3X_2]}$$

The a_1 , a_2 , & a_3 are constant coefficients that indicate whether the j^{th} variable is being added (by setting $a_j = +1$) or subtracted (by setting $a_j = -1$) from the rest of the variables.

Mood et al. /(1963, pages180-181) gives the following formulas for estimating the expected value and variance of two independent, random variables that are being multiplied together:

$$E[a_1X_1a_2X_2] = a_1E[X_1]a_2E[X_2]$$

$$\begin{aligned} Var[a_1X_1a_2X_2] &= (a_2E[X_2])^2a_1^2Var[X_1] + (a_1E[X_1])^2a_2^2Var[X_2] \\ &\quad + a_1^2Var[X_1]a_2^2Var[X_2] \end{aligned}$$

$$SD[a_1X_1a_2X_2] = a_1a_2\sqrt{Var[X_1X_2]}$$

APPENDIX B- CONFIDENCE INTERVAL FOR THE MEAN

Consider the case in which the confidence interval for the mean of variable X is wanted but the true variance of the distribution is not known and has to be estimated from the same data set. This is the situation with the mercury concentration and mercury load measurements taken at the sewer Plant. Mood et al. (1963, page 381-382) and Gilbert (1987, page 138) give the following formula for calculating the two-sided $100(1 - \alpha)\%$ confidence interval of the true mean using n values of data that are assumed to be normally distributed:

$$\left(Mean - t_{(1-\frac{1}{2}\alpha, n-1)} \frac{SD}{\sqrt{n}} \leq True Mean \leq Mean + t_{(1-\frac{1}{2}\alpha, n-1)} \frac{SD}{\sqrt{n}} \right).$$

This confidence interval formula for the mean can also be abbreviated into the more compact expression $Mean \pm t_{(1-\frac{1}{2}\alpha, n-1)} SD/\sqrt{n}$. The term n is the number of data measurements taken; the term SD is the standard deviation of the n values of data; term $Mean$ is the expected or mean value of the n values of data; α is the specified significance level (typically α is set as $\alpha = 0.05$, i.e., the 5% significance level); and $t_{(1-\frac{1}{2}\alpha, n-1)}$ is the cumulative one-sided Student's-t distribution function with $n-1$ degrees of freedom and a significance level α .

For example, if there are 31 data values, then the one-sided Student's-t distribution function $t_{(1-\frac{1}{2}\alpha, n-1)}$ for the 95% confidence interval is given as follows by Gilbert (1987, page 255):

$$\begin{aligned} n &= 31 \\ \alpha &= 0.05 \end{aligned}$$

$$\begin{aligned} t_{(1-\frac{1}{2}\alpha, n-1)} &= t_{(0.975, 30)} \\ &= 2.042 \end{aligned}$$

$$\left(Mean - 2.042 \frac{SD}{\sqrt{31}} \leq True\ Mean \leq Mean + 2.042 \frac{SD}{\sqrt{31}} \right).$$

This result can be expressed using the more compact notation, such that for this example with 31 data values:

$$Mean \pm 95\% CI = Mean \pm 2.042 \frac{SD}{\sqrt{31}}.$$

APPENDIX C- MANN-KENDALL TEST OF SLOPE FOR TREND SIGNIFICANCE AND THE SEASONAL KENDALL TEST

The Mann-Kendall test for trend is insensitive to the presence or absence of seasonality. It is a nonparametric test since it does not assume any type of data distribution. Nonetheless, two forms of the test are provided—one ignoring data seasonality even if it is present, and one considering data seasonality. In either test, the null hypothesis, H_0 , assumes that the trend is zero, and the alternate hypothesis, H_a , is that the trend is non-zero. Details of the Mann-Kendall trend test for slope and the seasonal Kendall trend test are shown below.

In general, the Mann-Kendall trend test considering seasonality indicates a larger range for an allowable estimate of trend when seasonality is actually present than the range indicated by the test performed ignoring seasonality.

In the Mann-Kendall trend analysis and Kendall seasonal analysis, the “Sen” slope is first calculated and then it is determined whether the slope is statistically significant. Slope is statistically significant if it is non-zero. The median value of the Sen slope is calculated with and without seasonality. Since slopes are calculated over all possible time intervals, it is possible that the test indicates a “non-zero” trend, yet the median slope value equal zero.

MANN-KENDALL TREND TEST FOR SLOPE

Mann-Kendall Trend Test for Slope Significance – for number of data as small as 10, unless there are many tied (e.g., equal, NDs are treated as tied) values (Gilbert, 1987; p. 208)

Indicator Function $\text{sgn}(x_j - x_k) = 1$ if $(x_j - x_k) > 0$

$\text{sgn}(x_j - x_k) = 0$ if $(x_j - x_k) = 0$

$\text{sgn}(x_j - x_k) = -1$ if $(x_j - x_k) < 0$

where x_1, x_2, \dots, x_n are the time ordered data (n is the total of data).

Mann-Kendall Statistic, $S = \sum_{k=1}^{n-1} \sum_{j=k+1}^n \text{sgn}(x_j - x_k)$

Variance of $S : \text{Var}(S)$

$$\text{Var}(S) = \frac{1}{18} \left[n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) - \sum_{q=1}^h u_q(u_q-1)(2u_q+5) \right]$$

$$+ \frac{\sum_{p=1}^{g_i} t_{ip}(t_{ip}-1)(t_{ip}-2)}{9n_i(n_i-1)(n_i-2)} \sum_{q=1}^{h_i} u_{iq}(u_{iq}-1)(u_{iq}-2)$$

$$+ \frac{\sum_{p=1}^{g_i} t_{ip}(t_{ip}-1) \sum_{q=1}^{h_i} u_{iq}(u_{iq}-1)}{2n_i(n_i-1)}$$

where g is the number of tied groups (equal-valued) in the data set; t_p is the number of tied data in the p -th group; h is the number of sampling times (or time periods) in the data set that contain multiple data; u_q is the number of multiple data in the q -th time period; and n is the number of data values.

Test Statistic,
 T_s

The Kendal statistic T_s is defined as

$$= \frac{S-1}{\sqrt{\text{Var}(S)}} \quad \text{if } S > 0$$

$$T_s = 0 \quad \text{if } S = 0$$

$$= \frac{S+1}{\sqrt{\text{Var}(S)}} \quad \text{if } S < 0$$

where a positive T_s value means an upward trend and a negative T_s value means a negative trend.

<p>Hypothesis Test: H_0 = no trend H_{a1} = upward trend present H_{a2} = downward trend present This is a one-sided test at the α significance level.</p>	<p>The null hypothesis H_0 assumes that there is no trend in the data as a function of time. However, we will check for two alternative hypotheses. These are determined as follows: A1) Reject the null hypothesis H_0 and accept the alternative hypothesis H_{a1} for an upward trend if $T_s > 0$ and $T_s > Z_{1-\alpha}$; A2) Reject the null hypothesis H_0 and accept the alternative hypothesis H_{a2} of a downward trend if $T_s < 0$ and $T_s > Z_{1-\alpha}$. The term $Z_{1-\alpha}$ is the cumulative normal distribution function, which can be obtained from Table A1 in Gilbert (1987; p. 254).</p>
<p>Sen's Slope Estimator: Q</p>	<p>Slopes are initially calculated over each possible time period: $Q_{lk} = \frac{X_l - X_k}{t_l - t_k}, l > k$ where X_l and X_k are the concentrations measured at time t_l and t_k. These Q_{lk} individual slopes are ranked, and the median value is used to represent the slope estimator of trend (Gilbert, 1987; p. 227).</p>

SEASONAL KENDALL TEST

Seasonal Kendall Test – for number of data as small as 10, unless there are many tied (e.g., equal, NDs are treated as being tied) values (Gilbert, 1987; p. 225)

$$\begin{aligned} \text{Indicator Function } \text{sgn}(x_{ij} - x_{jk}) &= 1 \text{ if } (x_{ij} - x_{ik}) > 0 \\ &= 0 \text{ if } \boxed{} \\ &= -1 \text{ if } (x_{ij} - x_{ik}) < 0 \end{aligned}$$

where $x_{i1}, x_{i2}, \dots, x_{in}$ are the time ordered data (n_i is total of data in the i-th season).

$$\text{Mann-Kendall Statistic, } S_i = \sum_{k=1}^{n_i-1} \sum_{j=k+1}^{n_i} \text{sgn}(x_{ij} - x_{ik})$$

$$\begin{aligned} \text{Variance of } S_i \quad \text{Var}(S_i) &= \frac{1}{18} \left[n_i (n_i - 1) (2n_i + 5) \right. \\ &\quad \left. - \sum_{p=1}^{g_i} t_{ip} (t_{ip} - 1) (2t_{ip} + 5) \right. \\ &\quad \left. - \sum_{q=1}^{h_i} u_{iq} (u_{iq} - 1) (2u_{iq} + 5) \right] \\ &\quad + \frac{\sum_{p=1}^{g_i} t_{ip} (t_{ip} - 1) (t_{ip} - 2)}{9 n_i (n_i - 1) (n_i - 2)} \sum_{q=1}^{h_i} u_{iq} (u_{iq} - 1) (u_{iq} - 2) \\ &\quad + \frac{\sum_{p=1}^{g_i} t_{ip} (t_{ip} - 1) \sum_{q=1}^{h_i} u_{iq} (u_{iq} - 1)}{2 n_i (n_i - 1)} \\ \text{Var}(S') &= \sum_{i=1}^l \text{Var}(S_i) \end{aligned}$$

where g_i is the number of tied groups (equal-valued) data in the i-th season, t_{ip} is the number of tied data in the p-th group for the i-th season, h_i is the number of sampling times (or time periods) in the i-th season that contain multiple data, u_{iq} is the number of multiple data in the q-th time period in the i-th season, and n_i is the number of data values in the i-th season.

Test Statistic, T_s	<p>if $S' = \sum_{i=1}^K S_i$, where K is the number of seasons, then</p> $= \frac{S'-1}{\sqrt{Var(S')}} \quad \text{if } S' > 0$ $T_s = 0 \quad \text{if } S' = 0$ $= \frac{S'+1}{\sqrt{Var(S')}} \quad \text{if } S' < 0$ <p>where a positive T_s value means an upward trend and a negative T_s value means a negative trend.</p>
<p>Hypothesis Test:</p> <p>H_0 = no trend</p> <p>H_{a1} = upward trend present</p> <p>H_{a2} = downward trend present</p> <p>This is a one-sided test at the α significance level.</p>	<p>The null hypothesis H_0 assumes that there is no trend in the data as a function of time after seasonal effects have been removed. However, we will check for two alternative hypotheses. These are determined as follows:</p> <p>A1) Reject the null hypothesis H_0 and accept the alternative hypothesis H_{a1} for an upward trend if $T_s > 0$ and $T_s > Z_{1-\alpha}$;</p> <p>A2) Reject the null hypothesis H_0 and accept the alternative hypothesis H_{a2} of a downward trend if $T_s < 0$ and $T_s > Z_{1-\alpha}$.</p> <p>The term $Z_{1-\alpha}$ is the cumulative normal distribution function, which can be obtained from Table A1 in Gilbert (1987; p. 254).</p>
Sen's Slope Estimator: Q_{ilk}	<p>Slopes are initially calculated for the ith season of the lth and kth years:</p> $Q_{ilk} = \frac{X_{il} - X_{ik}}{t_{il} - t_{ik}}, l > k$ <p>where X_{il} and X_{ik} are the concentrations measured in the ith season of years t_l and t_k. These Q_{ilk} individual slopes are ranked, and the median value is used to represent the seasonal slope estimate (Gilbert, 1987; p. 227).</p>

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